Influence of temperature on the photodegradation process using Ag-doped TiO2nanostructures: Negative impact with the nanofibers

Barakata, Nasser A.M.; Kanjwal, Muzafar Ahmad; Chronakis, Ioannis S.; Kim, H. Y.

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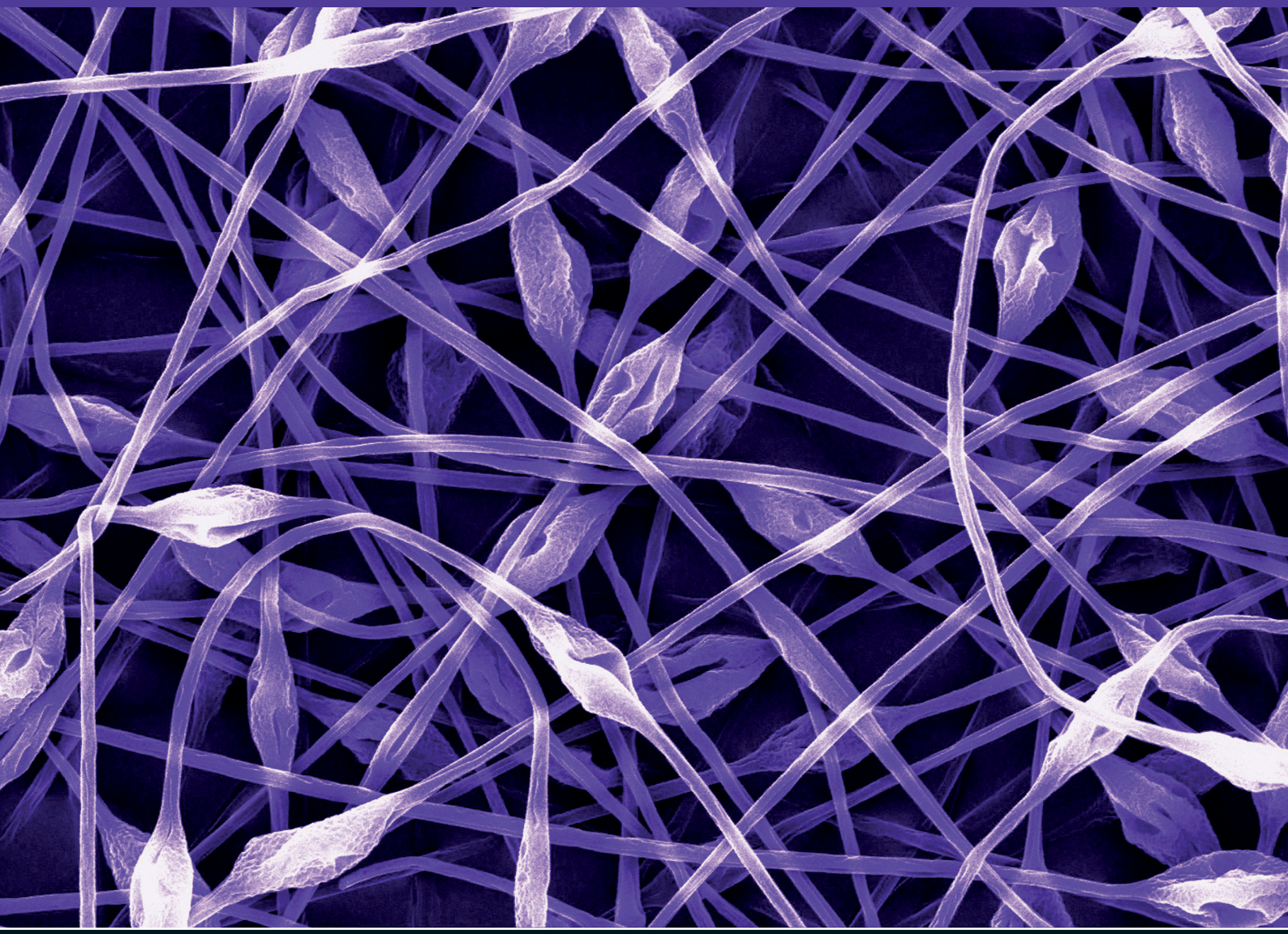

Electrospinning, Principles, Possibilities and Practice 2013

5 – 6 December 2013
Institute of Physics, London, UK

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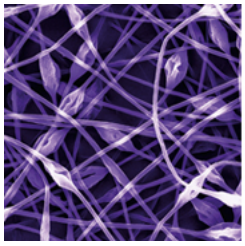

Electrospinning, Principles, Possibilities and Practice 2013

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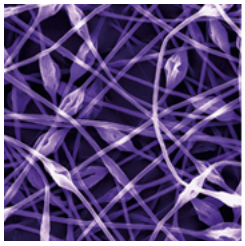


Electrospinning, Principles, Possibilities and Practice 2013

Programme

5-6 December 2013
Institute of Physics, London, UK

Thursday 5 December 2013

09:45 Registration and welcome refreshments
Hooke Room, 2nd Floor, Institute of Physics

10:15 **Welcome address**
Chairman: Professor Geoffrey Mitchell
Hooke Room, 2nd Floor, Institute of Physics

The Electrospinning Process

10:30 **(plenary) Opening lecture**
S Ramakrishna, National University of Singapore, Singapore

11:15 **Development of pulse electrospinning setup and getting micron length of fiber**
Y Aliyev, Institute of Combustion Problems, Kazakhstan

11:40 **Effect of chain entanglements on electrospun poly lactic acid (PLA) fibres**
R Casasola, Loughborough University, UK

12:05 **Recent advances in colloid-electrospinning**
D Crespy, Max Planck Institute for Polymer Research, Germany

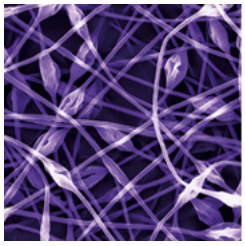
12:30 Lunch
Abdus Salam Room, 2nd Floor, Institute of Physics

13:30 **(invited) Polymer network in a strong extensional flow - A study of the electrospinning jet**
E Zussman, Technion - Israel Institute of Technology, Israel
Hooke Room, 2nd Floor, Institute of Physics

13:55 **Presentation tbc**

14:20 **High-throughput slit-surface electrospinning of core-sheath fibers**
Q Pham, Arsenal Medical, USA

14:45 **Molecular insight into the NanoSpider technology from computer simulations**
F Moucka, J E Purkinje University, Czech Republic



Electrospinning, Principles, Possibilities and Practice 2013

15:10 **3D and nanoscale investigations of wetting between organic liquids and electrospun nanofibre networks**
U Stachewicz, Nanoforce Technology Ltd., UK

15:35 Refreshment break
Abdus Salam Room, 2nd Floor, Institute of Physics

Melt Electrospinning
Hooke Room, 2nd Floor, Institute of Physics

16:00 **(invited) Melt Electrospinning - The return of a forgotten Polymer Processing Technology**
D W Hutchmacher, Queensland University of Technology, Australia

16:45 **Determination of nanofibrous layers homogeneity by means of imaging Raman spectroscopy**
A Kotzianova, Contipro Biotech s.r.o., Czech Republic

17:10 **Anomaly in temperature response of electrospun polyurethane nanofibers**
A Arinstein, Technion – Israel Institute of Technology, Israel

17:35 **Graphene/TiO2 based catalysts on nanostructured membranes: moving towards advanced solution for VOCs control**
M Roso, University of Padova, Italy

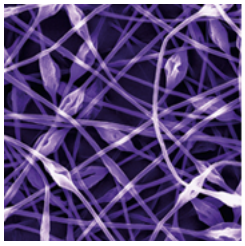
18:00 **The history of the science and technology of electrospinning from 1600 to 1995**
N Tucker, The New Zealand Institute for Plant and Food Research Ltd, New Zealand

18:45 Delegates to be led to the Royal Institute of British Architects (RIBA) – journey time 2 minutes walk

18:55 **Poster Snap Shots**
Chairman: Professor Geoffrey Mitchell
Wren Room, Royal Institute of British of British Architects (RIBA)

19:25 **Poster session, drinks reception and buffet dinner**

21:00 Close of day one



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Friday 6 December 2013

09:00 **(invited) 3D Printing using Melt Electrospinning**
P Dalton, Queensland University of Technology, Australia
Hooke Room, 2nd Floor, Institute of Physics

Melt ES & TE
Hooke Room, 2nd Floor, Institute of Physics

09:45 **Presentation tbc**

10:10 **Highly aligned electrospun platforms for skeletal muscle differentiation**
V Guarino, IMCB/CNR, Italy

10:35 **Polysaccharide based nanofibres containing curcumin for antibacterial dressing**
A Hébraud, ICPEES / University of Strasbourg, France

11:00 Refreshment break

Melt ES & TE (continued…)
Hooke Room, 2nd Floor, Institute of Physics

11:30 **Electrospun nanofibers applied for tissue engineering and medical therapies**
T Kowalczyk, Polish Academy of Sciences, Poland

11:55 **Electrospun core-sheath PEO/Eudragit S100 nanofibers for enhanced magnetic resonance imaging**
M Jin, University College London School of Pharmacy, UK

Applications
Guthrie Room, 1st Floor, Institute of Physics

09:45 **Electrospinning research at Rhodes University**
S Chigome, Rhodes University, South Africa

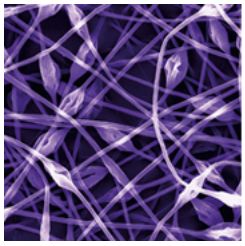
10:10 **Influence of temperature on the photodegradation process using Ag-doped TiO2nanostructures: Negative impact with the nanofibers**
M Kanjwal, DTU Food, Denmark

10:35 **Applications of electrospinning of biopolymers in the food and food packaging areas**
J Lagaron, CSIC, Spain

Biological
Guthrie Room, 1st Floor, Institute of Physics

11:30 **Bioactive electrospun fish sarcoplasmic proteins - A potential oral delivery system**
K Stephansen, Technical University of Denmark, Denmark

11:55 **Functional nanofibers based on natural polymers**
E Mele, Italian Institute of Technology, Italy



Electrospinning, Principles, Possibilities and Practice 2013

12:20 **Electrospun, cross-linked poly(aspartic acid) based fiber matrix: Preparation and biological application**
K Molnár, Semmelweis University, Hungary

12:45 **Presentation tbc**

13:10 **Development of bio-compatible polymer films via electrospinning for use as synthetic membranes to cure retinal degeneration**
G Ward, University of Southampton, UK

12:20 **Tailoring electroactive response of poly(vinylidene fluoride) electrospun membranes for tissue engineering applications**
V Sencadas, University of Minho, Portugal

12:45 **In vivo response of bicomponent electrospun conduits for peripheral nerve regeneration**
V Cirillo, IMCB/CNR, Italy

13:10 *No presentation scheduled*

13:35 Lunch
Abdus Salam Room, 2nd Floor, Institute of Physics

S & P & Applications
Hooke Room, 2nd Floor, Institute of Physics

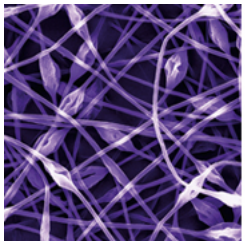
14:15 **(invited) Nanofibres and nanoparticulates**
F Davis, University of Reading, UK

14:50 **SANS study of chain conformation and relaxation kinetics of electrospun polystyrene fibers**
A Lancuski, Université Joseph Fourier, France

15:15 **SANS study of electrospun polymer fibres**
S Mohan. University of Reading, UK

15:40 **Supercapacitance from carbonised cellulose nanofibres**
S Eichhorn, University of Exeter, UK

16:05 Refreshment break
Abdus Salam Room, 2nd Floor, Institute of Physics



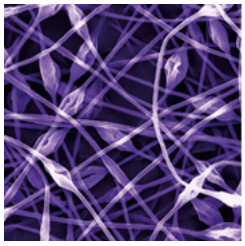
Electrospinning, Principles, Possibilities and Practice 2013

Electrospun Plus
Chairman: Professor Geoffrey Mitchell
Hooke Room, 2nd Floor, Institute of Physics

16:30 **Tough electrospun polystyrene nanocomposites**
A Barber, Queen Mary University of London, UK

17: 00 **Controlling the pore size of 3D electrospun biomaterials using simultaneously and synergistically electrospinning, electrospraying and architectured collectors**
C Wittmer, Université de Strasbourg, France

17:30 Close of day two and conference



Electrospinning, Principles, Possibilities and Practice 2013

Poster Programme

P.01 Enhancing the optical properties of silicon quantum dots using silver nanoparticles
K Abualnaja, Newcasatle University, UK

P.02 The effect of humidity on the electrospinning of Poly(vinyl alcohol)
M Aumonier, WMG, UK

P.03 Electrospinning of nanofibrous materials for fuel cell applications
S Cavaliere, ICGM/University Montpellier 2, France

P.04 Multifunctional nanocomposites: The use of filled electropun fibers as functional modifier
G Cicala, University of Catania, Italy

P.05 In Vitro investigation of human cell viability, proliferation, and migration on a biodegradable 3D-electrospun scaffold
C Craig, University of Tulsa, USA

P.06 Metal and metal oxide electrospun nanowires for PEMFC applications
G Ercolano, University of Montpellier 2, France

P.07 Design of multifunctional µ-carriers by electric field-assisted atomization
V Guarino, IMCB/CNR, Italy

P.08 Morphological investigationof PCL and gelatin fibres in simulated culture conditions
V Guarino, IMCB/CNR, Italy

P.09 Nanofibrous nonwoven mats of poly(ethylene terephthalate)/poly(lactic acid) blends with covalently attached trypsin
A Guiomar, Universidade de Coimbra, Portugal

P.10 Core-shell carbon-ceramic fibres by electrospinning and atomic layer deposition (ALD) for fuel cell catalyst supports
P Heikkilä, VTT Technical Research Centre of Finland, Finland

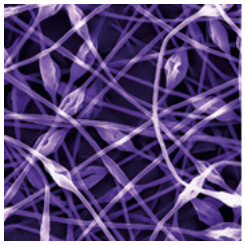
P.11 Optical noninvasive method for rapid determination of alignment degree of oriented nanofibrous layers
J Klemes, Contipro Biotech s.r.o., Czech Republic

P.12 Electrospun PAN/PVDF composite for Li-ion battery separator
Y Liu, Tianjin Polytechnic University, China

P.13 Electrospinning polymers for tissue engineering applications
Z McCrea, PhD Student, Ireland

P.14 Development of orientation during electrospinning of fibres of poly(ε-caprolactone)
G Mitchell, Institute Polytechnic Leiria, Portugal

P.15 Electrospun polyethylene oxide fibres containing carbon nanotubes
M Nazhipkyzy, University of Reading, al-Farabi Kazakh National University, UK



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P.16 Fibrous scaffolds for neural tissue engineering in the auditory system
K Ngamkham, University College London, UK

P.17 Regulation and safety mechanisms of the 4SPIN® technology
M Pokorny, Contipro Biotech s.r.o., Czech Republic

P.18 Introduction of new laboratory device 4SPIN® for nanotechnologies
M Pokorny, Contipro Biotech s.r.o., Czech Republic

P.19 Production of $GdBa_2Cu_3O_7$-x nanofibers by electrospinning method
A Qalambor Dezful, Shahid Chamran University, Iran

P.20 Study on stabilization of electrospun polyacrylonitrile nanofibers as carbon nanofibers precursor in different temperatures
A Qalambor Dezful, Shahid Chamran University, Iran

P.21 Study on the effect of diameter size of electrospun ZnO nanofibers as a photo anode on the efficiency of CdS Quantum dot sensitized solar cells (QDSSCs)
A Qalambor Dezful, Shahid Chamran University, Iran

P.22 Production of composite nanomaterials using 4SPIN® technology
J Rebicek, Contipro Biotech s.r.o., Czech Republic

P.23 Electrospinning of hyaluronic acid by 4Spin® technology
J Ruzickova, Contipro Biotech s.r.o., Czech Republic

P.24 Effect of NaY zeolite content on electrospun PVDF/NaY fiber meshes membranes for biomedical applications
V Sencadas, University of Minho, Portugal

P.25 Electrospun silk-elastin-like fiber mats with potential application for tissue engineering
V Sencadas, University of Minho, Portugal

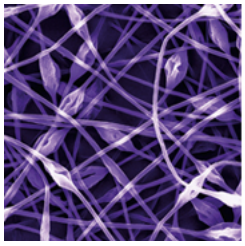
P.26 Structural and morphological control of electrospun polymer and carbon nanofibers
C S Sharma, Indian Institute of Technology Hyderabad, India

P.27 In-situ measurement of adhesion between electrospun fibers
U Stachewicz, Nanoforce Technology Ltd., UK

P.28 Composite electrospun nanofibres for treatments of air and water
C Tonetti, CNR-ISMAC, Italy

P.29 Growth of nanosized-copper benzene-1,3,5-tricarboxylate on electrospun crosslinked polyvinyl alcohol-polyacrylic acid membrane
Y Truong, CSIRO Materials Science and Engineering, Australia

P.30 Atomic force microscopy and nanoindentation techniques for fast and effective control over the structure and mechanical properties of electrospun nanofiber mesh
Y Tsekov, Bulgarian Academy of Sciences, Bulgaria



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P.31 Methods for measuring electrospun fibre diameters
N Tucker, Plant and Food Research Ltd., New Zealand

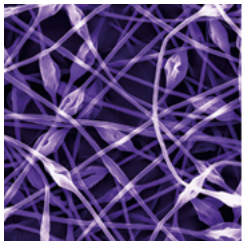
P.32 Addressing issues of electrospinning nanofibres on textiles: Productivity, perturbation and adhesion
A Varesano, CNR-ISMAC, Italy

P.33 Electrospinning of keratin/hydroxyapatite nanofibre scaffolds for bone tissue engineering
C Vineis, CNR-ISMAC Biella, Italy

P.34 Biodegradable nanocomposites via electrospinning
A Wooldridge, WMG, UK

P.35 Size dependent mechanical properties of electrospun polystyrene fibres
F Zhang, Queen Mary University of London, UK

P.36 Understanding oil repellent mechanisms in electrospun fibre networks
H Zhang, Queen Mary University of London, UK



Electrospinning, Principles, Possibilities and Practice 2013

Oral Abstracts

Thursday 5 December 2013

The Electrospinning Process

(invited) IOP London Electrospinning conference 2013 – Opening address

S Ramakrishna

National University of Singapore, Singapore

Electrospinning produces continuous fibers with thickness in the range of 1000 nm to 50 nm, and electrospraying produces particles with diameters in the range of 500 nm to 50 nm. These techniques are integrated to produce unique composite materials. Electrospun materials offer favourable properties including enhanced mechanical properties, surface-to-volume ratio, variations in wetting behaviour, tailored biological response, permeability, charge transport characteristics. Electrospun materials organised in two and three dimensioins are particularly interesting for enhancing the performance of various applications in healthcare (regenerative medicine, reprogramming of cells, drug delivery, stem cells and implants), wellbeing (nutrition, food & health supplements), recreation (light weight structures, fouling & bacteria resistant coatings & surfaces), energy (harvesting, storage, & efficiency), environment (air pollution control and water treatment). Hence the last ten years saw worldwide growth of R&D on various uses of electropsun materials. Where do we go from here? What do we need to overcome to make further progress?

Development of pulse electrospinning setup and getting micron length of fiber

Y T Aliyev, B M Dabynov, Z G Ospanova and Z A Mansurov

Institute of Combustion Problems, Republic of Kazakhstan

With conventional electrospinning method to obtain short fibers is problematic, the use of which is important in those problems where it is required a homogeneous mixing of fibers with other chemicals.

The aim of this work is the development and construction of the pulse electrospinning setup to produce nano-sized particles, with the ability to control their size. The prefix "nano" means that the dimensions of the particles to range from 10 to 500 nm in at least one dimension.

The prototype of the pulse electrospinning setup is a classic electrospinning setup, which operates at a constant voltage. In the pulse electrospinning setup unlike classical setup high voltage is applied in the form of controlled pulses, which allows to obtain a controlled fiber length.

An attempt was done in Canada to develop a setup of pulse electrospinning (2010y). However, in this setup, there was a technical limitation on the pulse value that arises due to the necessity of selecting high-voltage transistors with the same parameters (the authors used an insulated gate bipolar transistor). The maximum amplitude reached by the authors of the work does not exceed 10 kV, which is not possible to obtain short fibers.

We have designed and developed a pulse electrospinning setup, which has a higher amplitude of the high voltage - 16 kV (which is 6 kV more than the above settings). In the present apparatus for producing a pulsed high-voltage high-frequency transformer is used. A schematic diagram and photo of pulse electrospinning setup is showed.

The results lead to the following conclusions:

- a high-voltage pulse electrospinning setup was created which has a maximum voltage more than 16 kV;
- experimentally obtained short fibers of cellulose acetate having a diameter of 500 nm and a length of 5 micrometer;

Effect of chain entanglements on electrospun poly lactic acid (PLA) fibres

R Casasola, N L Thomas and S Georgiadou

Loughborough University, UK

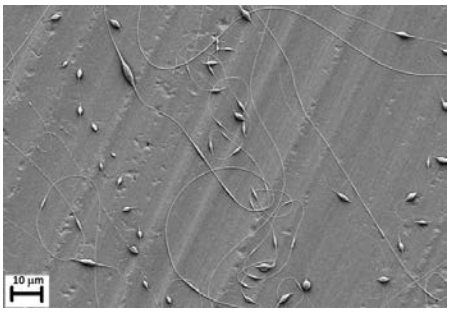
In a preliminary study the effect of different solvent systems on PLA nanofibre morphology and mean diameter has been investigated. PLA solutions were prepared by dissolving PLA in various pure solvents and binary-solvent systems. The most promising solvent system was acetone/dimethylformamide at a 50/50 v/v ratio generating defect-free nanofibres with a diameter of about 400 nm. In the current study the effect of PLA concentration in AC/DMF solutions on nanofibre morphology was investigated. Viscosity, conductivity and surface tension of the various solutions were measured. The electrospun fibres were examined using scanning electron microscopy (FEG-SEM) and image analysis software was used to measure the nanofibre diameter.

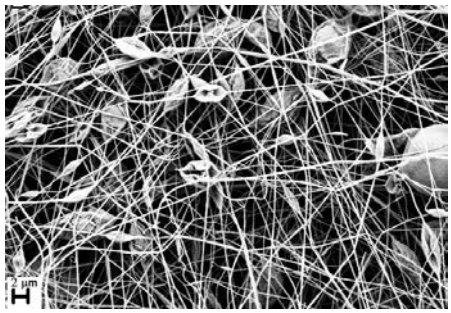
Polymer chain entanglements play a vital role in determining the structure in the electrospun polymer. Hence in this study the entanglement concentration, C_e, which allows the production of nanofibres, was measured by analysing the dependence of specific viscosity on polymer concentration. Experimental observations have shown that a minimum level of chain entanglements, and therefore a minimum concentration, is required for the production of continuous fibres. Increasing the concentration of polymer in solution increases chain entanglements and hence viscosity. Consequently during the electrospinning process the polymeric jet is stabilized due to the restricted motion of the polymer chains.

Results and discussion

Analysis of the dependence of specific viscosity on polymer concentration enabled the transition from the unentangled to the entangled state to be evaluated. The solvent system used this study gave an entanglement concentration C_e of 6% w/v. This was confirmed by SEM images, which showed that nanofibres could not be produced from PLA solution at 5% w/v, as in Figure 1(a), which shows that only droplets (beads) of the polymeric solution were collected. Beads formation indicates insufficient chain entanglement. Hence the study was not extended to concentrations below 5% w/v PLA. On increasing the polymer concentration to 7.5% w/v more nanofibres were produced even though a lot of beads were still present, as shown in Figure 1(b). From the logarithmic plot of viscosity as a function of the polymer concentration a steep increase at the C_e was observed due to extensive chain entanglements. The PLA nanofibres contained beads up to a concentration of 10% w/v. Above 12.5% w/v defect-free fibres could be collected as shown in Figure 1(c). Defect-free nanofibres with diameter of 462±125nm were obtained when the concentration increased to about twice that of C_e.

The results obtained suggested and confirmed that chain entanglements, and therefore solution concentration and solution viscosity have a significant effect on nanofibre morphology.

a.) 

b.) 

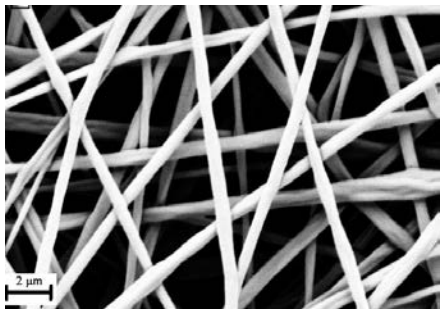
c.) 

Figure 1- Effect of PLA concentration in AC/DMF (50/50 v/v) solutions

Recent advances in colloid-electrospinning

D Crespy

Max Planck Institute for Polymer Research, Germany

An interesting recent variant of electrospinning, called colloid-electrospinning,[1-2] is applied to immobilize and/or assemble nanoparticles into nano- or microfibers, hence yielding multicompartment materials.
We discuss the preparation and characterization of fibers with solid or liquid nano-compartments obtained by the electrospinning of nanoparticles (Figure 1a) or emulsions with a focus on the latter. Applications of such materials include the fabrication of anisotropic particles (Figure 1b-c),[3-4] catalysis,[5] and energy conversion.[6]

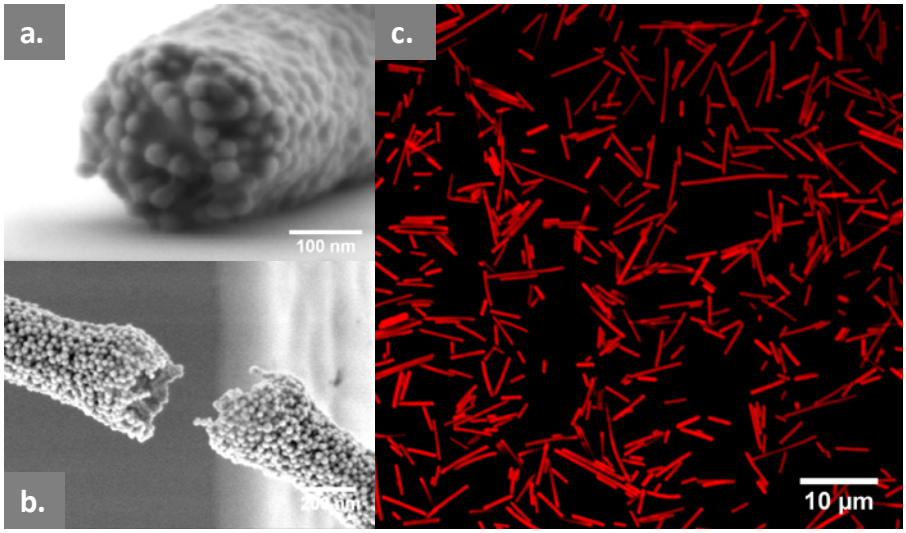


Fig. 1 SEM micrographs of a: a typical fiber obtained by colloid-electrospinning with high content of inorganic nanoparticles, b: fibers with structural and sacrificial compartments after removal of the latter. c: Fluorescent microscopy image of fluorescent silica microrods obtained by the simultaneous electrospinning of structural and sacrificial particular compartments.

[1] Crespy D., Friedemann, K., Popa A.M. 2012. Macromol. Rapid Commun. 23:1978.
[2] Friedemann K., Turshatov A., Landfester K., Crespy D. 2011. Langmuir 27:7132.
[3] Herrmann C, Turshatov A, Crespy D. 2012. ACS Macro Lett. 1:907.
[4] Friedemann K, Corrales T, Kappl M, Landfester K. 2012. Small 8:144.
[5] Horzum N, Munoz-Espi R, Glasser G, Demir M.M., Landfester K, Crespy D. 2012. ACS Appl. Mater. Interf. 4:6338.
[6] Wohnhaas, C., Friedemann, K., Busko, D., Landfester, K., Baluschev, S., Crespy, D., Turshatov, A. 2013. ACS Macro Lett. DOI:10.1021/mz400100j.

Melt Electrospinning

(invited) Polymer network in a strong extensional flow - A study of the electrospinning jet

I Greenfeld, A Arinstein and E Zussman

Technion- Israel Institute of Technology, Israel

The flow field in the electrospinning jet is typically governed by high strain rate extensional flow of a semi-dilute polymer solution that can cause substantial stretching and disentanglement of the polymer network. Modeling of the dynamic evolution of the entangled polymer network in an electrospinning jet predicted substantial longitudinal stretching and radial contraction of the network, a transformation from an equilibrium state to an almost fully-stretched state. This prediction was verified by X-ray phase-contrast imaging of electrospinning jets, which revealed a noticeable increase in polymer concentration at the jet center, within a short distance from the jet start. The model was expanded to semi-flexible conjugated polymer chains, and scanning near field optical microscopy (SNOM) of electrospun nanofibers revealed that the network's dense elongated conformation effectively remains after jet solidification. Furthermore, polymer entanglement loss in consequence of stretching was evidenced in jet fragmentation and appearance of short nanofibers. It was found that short nanofibers are likely to appear when a combination of low entanglement of the polymer chains and high strain rate of the electrospinning jet exist.

[1] I. Greenfeld, A. Arinstein, K. Fezzaa, M.H. Rafailovich, E. Zussman, “Dynamics of Polymers in Semi-Dilute Solution during Electrospinning: A Simple Model and Experimental Observations,” *Physical Review E*, 84, 2011.
[2] I. Greenfeld, K. Fezzaa, M.H. Rafailovich, E. Zussman, “Fast X-ray phase-contrast imaging of electrospinning polymer jets: measurements of radius, velocity and concentration,” *Macromolecules*, 45, 2012.
[3] I. Greenfeld, E. Zussman, “Polymer entanglement loss in extensional flow – evidence from electrospun short nanofibers,” *Journal of Polymer Science Part B: Polymer Physics*, 2013.

Electrospinning, Principles, Possibilities and Practice 2013

High-throughput slit-surface electrospinning of core-sheath fibers

X Yan[1], A Deleault[1], J Marini[1], R Mulligan[1], U Sharma[1], M Brenner[2], G Rutledge[3], T Freyman[1] and Q Pham[1]

[1]Arsenal Medical, USA, [2]Harvard University, USA, [3]Massachusetts Institute of Technology, USA

Core-sheath fibers fabricated via electrospinning show great promise for use in a variety of applications including drug delivery/tissue engineering, wound dressings, filters, and super-hydrophobic materials. However, needle-based, core-sheath electrospinning systems typically operate at flow rates between 1-10 mL/h, resulting in low throughput and deposition rate. We have recently developed a novel electrospinning process that uses a slit-fixture capable of producing core-sheath fibers at throughput rates significantly above that of traditional needle-based systems, thereby addressing current industrial manufacturing limitations. The slit-fixture is formed *via* alignment of two triangular-shaped nozzles along a single vertical plane. Core and sheath polymer solutions are delivered to the slits resulting in co-localization along the nozzle. Application of an electric field leads to spontaneous formation of multiple core-sheath jets. Specifically, upon activation of the electric field, sheath electrospinning jets emit along the length of the slit, resulting in a pressure drop at these locations; as a result, core fluid along the slit preferentially becomes entrained within the sheath jet. We have investigated and will discuss the impact of flow rate, fluid properties, voltage, and slit design on this process, with an emphasis on process stability and control over core-sheath Taylor cone jet morphology. The data indicate that manipulation of these variables to increase the ratio between the sheath and core (1) fluid flow velocity and/or (2) viscosity result in the formation of Taylor cones with more distinct core/sheath morphologies, which we hypothesize results in better core-sheath fiber structure.

Additionally, we have observed improved process stability via modulation of jet number, either through increasing voltage or slit-design. To date, using a 14 cm long slit fixture, we have demonstrated production of core-sheath micro- and nanofibers at total flow rates in excess of 1000 mL/h using various material systems (depending on the concentration of the solution, this benchmark translates to 50-200 grams of material per hour). Preliminary data indicate that fiber diameter size, uniformity, and distribution are on par with needle-based electrospinning processes. And as with needle-based coaxial electrospinning, the slit-fixture also allows the fabrication of fibers that are particle-encapsulating, bicomponent, hollow, or not normally electrospinnable. This technology has the potential to provide core-sheath micro and nanofiber production at rates sufficient to commercialize a number of novel products.

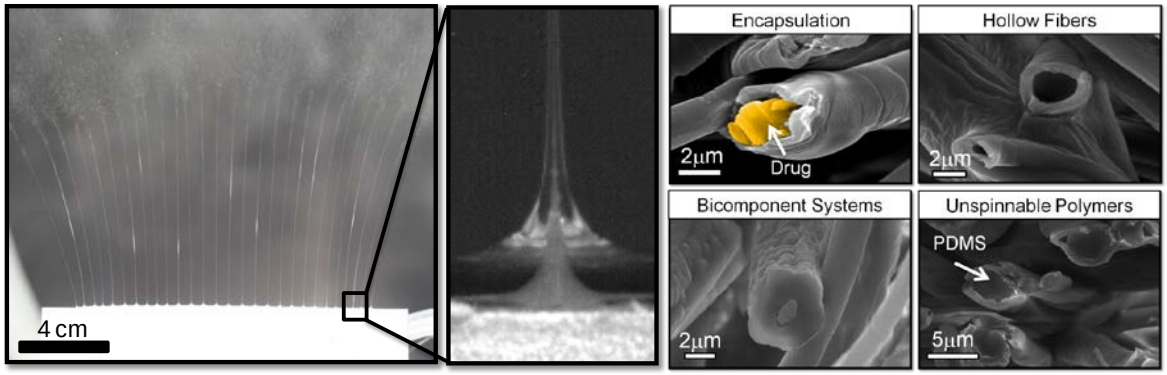
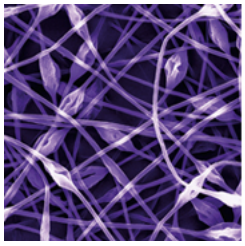


Fig 1. (Left) Image showing multiple core-sheath electrospinning jets emitted from a 14 cm long slit surface. (Middle) Close-up image of individual electrospinning jet depicting core-sheath morphology. (Right) Examples of different types of core-sheath fibers fabricated using a slit-fixture.



Electrospinning, Principles, Possibilities and Practice 2013

Application of computer simulations: Molecular understanding of electrospinning

I Nezbeda, F Moucka and J Jirsak

J. E. Purkinje University, Czech Republic

Nanospider technology is a method to produce nanofibers by electrospinning from the free surface of polymer solutions. Due to the lack of understanding of the process on the molecular level, the actual setup of the process (strength of the electric field, composition of the solution, temperature, etc.) has been based so far on the trial-and-error.

In the presentation the process will be briefly described, the main problems identified, and the role of molecular simulations (i) to understand what is going on in the system during the spinning and (ii) to reveal relations between various molecular and/or thermodynamic properties affecting the process detailed.

We report first simulation results focussing on the interplay between the ions, electric field and water molecules, and on the onset of the surface waves and the origin of the Taylor cones. Furthermore, of a particular interest is the orientational arrangement of the water molecules in the interphase layer because this arrangement seems to be responsible for all the observed phenomena.

All these results provide the necessary input information into semiempirical and theoretical macroscopic methods leading to improved efficiency of the production.

3D and nanoscale investigations of wetting between organic liquids and electrospun nanofibre networks

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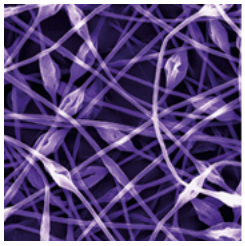
The wetting behaviour between electrospun nanofibrous networks and liquids is of critical importance in many applications including filtration and liquid repellent textiles. However, understanding the relationship between nanofibre properties, including surface characteristics as well as the fibre's geometric organization, and resultant wetting characteristics of the nanofibre network is yet to be accurately determined. This work uses novel 3D imaging exploiting focussed ion beam (FIB) microscopy and cryo-scanning electron microscopy (cryo-SEM) to highlight a wetting hierarchy that defines liquid interactions with the network. Specifically, small length scale wetting between individual electron nanofibres and liquid, measured both using direct SEM visualisation and a Wilhelmy balance approach, is observed to differ when compared to larger scale liquid droplet shapes. These observations are important in defining general rules for understanding the wetting behaviour between liquid droplets for future electrospun nanofibre applications. We finally exploit this understanding to design a porous electrospun nanofibre network that is effectively acting as an oleophobic surface for the demanding application of repelling low surface tension liquids.



Electrospinning, Principles, Possibilities and Practice 2013

Determination of nanofibrous layers homogeneity by means of imaging Raman spectroscopy

A Kotzianova[1,2], J Klemes[1], J Rebicek[1], M Pokorny[1], P Mojzes[3], J Palacky[3] and V Vladimir[1]

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Nanofibrous materials with composite structure are in high demand, especially for applications in the field of biomedicine. By using a combination of materials we are able to enhance the properties of the final product or incorporate active substances in its nanofibrous structure. The finished nanofibrous material can be composed of different individual layers of various materials or be made up of individual entangled nanofibers of various materials.

Randomly mixed meshes are commonly prepared using a multiple needle system where each needle contains a different solution. When a static collector is used repulsive forces cause inhomogeneity in the produced layers. However, homogeneity may be enhanced using a rotating drum collector.

The degree of homogeneity, an important property of the final nanofibrous structure, can be measured by Raman spectroscopy. Raman spectroscopy was used to analyse nanofibrous layers consisted of different types of polymers. A custom-developed laboratory confocal Raman apparatus was used for the analysis. The homogeneity of the samples, prepared under different conditions, was determined by imaging their chemical structure distribution on the basis of the Raman spectrum. Furthermore a statistical method, specifically factor analysis, was used to distinguish between the contributions of each polymer to the cumulative spectra.

Anomaly in temperature response of electrospun polyurethane nanofibers

A Arinstein, D Alhazov, M Burman, and E Zussman

Technion Israel Institute of Technology, Israel

Thermo-mechanical study of electrospun nanofibers, fabricated of thermoplastic polyurethane block co-polymer (TPU) containing soft and hard segments (T_g ~50°C), is presented. When measuring the strain of fiber mat as a function of the temperature we observed that at a certain temperature (70~80°C) they start to massively contract, whereas TPU cast films started to ex- pand in the same temperature range (see Fig. 1). The strain response of fiber mat and cast film in isothermal conditions (90°C) also differs dramatically. As expected the film sample ex- panded, while the fiber mat sample began to contract at ~70°C, and last for ~100 min. At that moment, the contraction stopped and the strain kept nearly constant at ~40% for approximately 200 min. Then, the fiber mat started to expand (see Fig. 2). TPU single nanofibers also demonstrate an isothermal contraction. The effect depends both on spinning conditions and on the experiment temperature (see Fig. 3). Nevertheless, the observed phenomenon cannot be attributed to confinement effect, as cast films also demonstrate a contraction after high- temperature stretching (see Fig. 4).

Note that in all long time-exposure experiments the material didn't flow, and at the same time the soft part of TPU matrix is above T_g, i.e., relaxation to equilibrium is possible.

Based on blob concept, a model describing TPU matrix microstructure preventing a relaxation of stretch material is proposed.

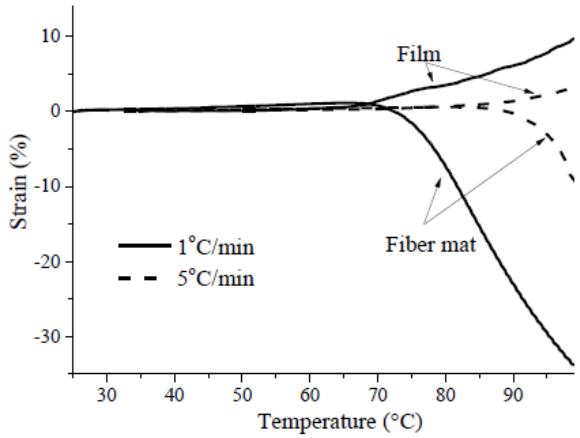


Figure 1. The strain vs. temperature response of TPU electrospun fibers and cast film.

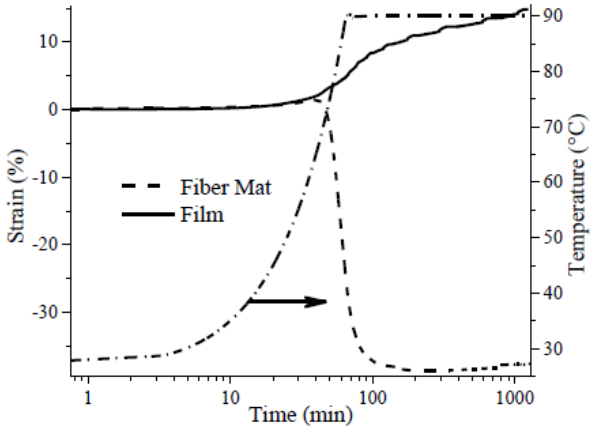


Figure 2. The strain response vs. time of fiber mat and cast film in isothermal conditions at 90°C.

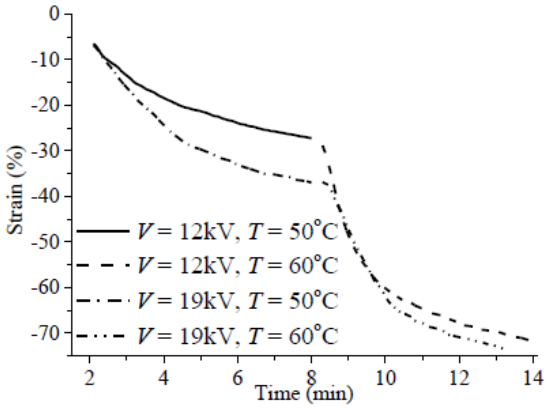


Figure 3. Contraction phenomena in individual TPU nanofibers.

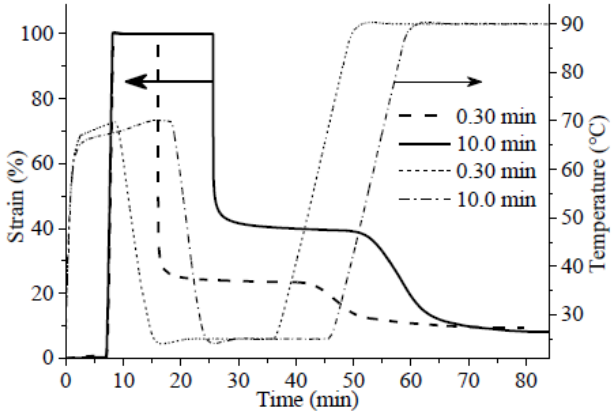


Figure 4. Contraction phenomena in TPU cast film after high-temperature stretching.

Graphene/TiO_2 based catalysts on nanostructured membranes: Moving towards advanced solution for VOCs control

M Roso, N Pozzan, C Boaretti, A Lorenzetti, S Besco and M Modesti

University of Padova, Italy

People's lifestyle gradually changed in the last century because they generally spend more than 80% of their time in an indoor environment such as home, office, car and shopping centre. Within this scenario the Indoor air quality (IAQ) has become an important community concern because there is a sufficient evidence of an association between indoor dampness-related factors and a wide range of respiratory or allergic health effects, including asthma, cough, respiratory infections, bronchitis, allergic rhinitis, to cite some examples.

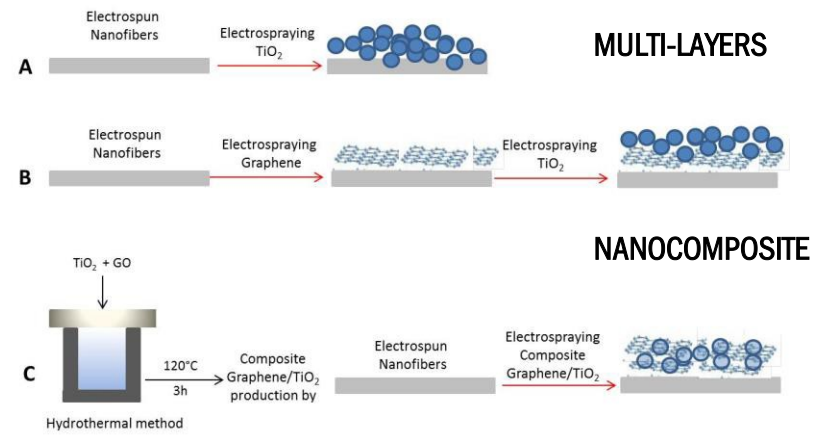
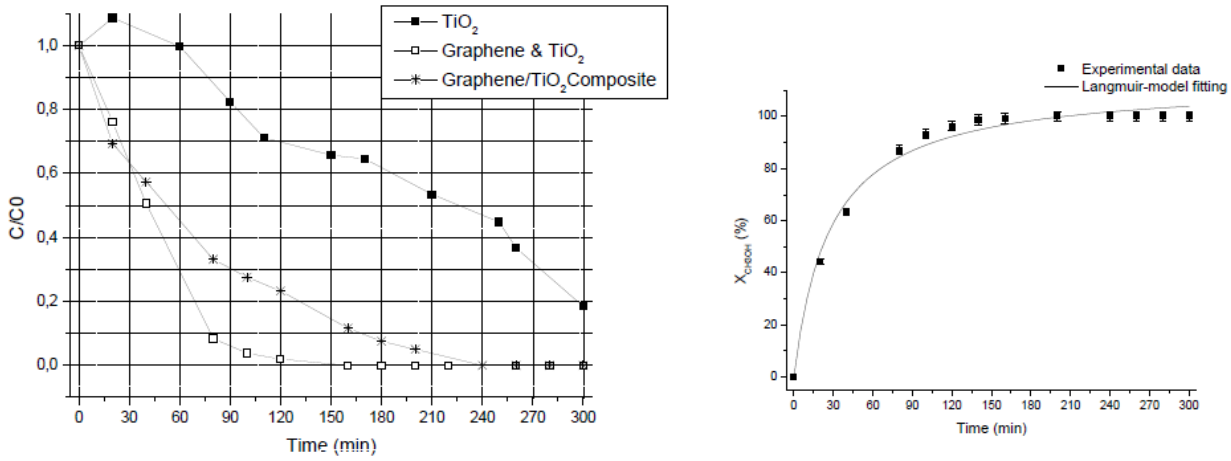


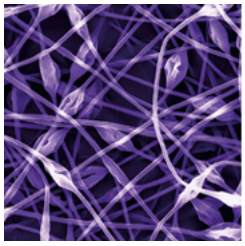
Figure 1 Scheme of the proposed membranes

According to this, the development of new solutions in pollution sensing and prevention by using adequate nanostructures with unique properties has gained more interest in the scientific community. The present work is meant to show the production, characterization and the catalytic performance of nanostructured membranes based on electrospun polyacrylonirile (PAN) scaffolds and graphene/titania based catalysts. Three different systems of catalyst were chosen in order to compare their photocatalytic properties: neat TiO^2, TiO^2 plus graphene and TiO^2/graphene composite obtained by hydrothermal method from graphene oxide as shown in Fig. 1. Results of the photocatalytic performance on methanol gas-phase degradation (Fig.2 (a)), revealed a higher reaction rate of the graphene based catalysts wherein an effective charge transfer, enhanced by graphene, has been supposed to reduce the charge recombination increasing the photocatalytic activity of TiO^2 nanoparticles. More in detail, nanocomposite membrane, resulted on further improvement of the photocatalytic performance when the tests were carried out for longer experiment time, in good agreement with the Langmuir-Hinshelwood kinetic, as shown in Fig.2 (b).



(a) (b)

Figure 2 (a) Photocatalytic performance of the tested membranes; (b) L-H model fitting for membrane Type C, NANOCOMPOSITE



Electrospinning, Principles, Possibilities and Practice 2013

The history of the science and technology of electrospinning from 1600 to 1995

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[1]The New Zealand Institute for Plant and Food Research, New Zealand, [2]University of Canterbury, New Zealand

Electrospinning is a dry spinning process that uses electrostatic force to draw fibres from a liquid polymer solution or melt. The process of fibre formation from the liquid is entirely physical either by loss of solvent or freezing of a melt. The process has recently achieved widespread popularity in the laboratory as a method for the manufacture of continuous nano-scale fibres. There is also a well-established industry using electrospinning to manufacture high efficiency filters.

This paper outlines the story of electrostatic production and drawing of fibres: electrospinning. In 1600, the first record of the electrostatic attraction of liquids was observed by William Gilbert. In 1887 Charles Vernon Boys described the process. John Francis Cooley filed the first patent in 1900. Between 1931 and 1944 Anton Formhals took out at least 22 patents on electrospinning. In 1938, N.D. Rozenblum and I.V. Petryanov-Sokolov generated electrospun fibres, and developed them into filter materials. In the early 1990s several research groups (notably that of Reneker [1] who popularised the name electrospinning for the process) demonstrated that many organic polymers could be electrospun into nanofibers. Since then, the number of publications about electrospinning has been increasing exponentially every year

An earlier version of this paper is available for download at
www.jeffjournal.org/papers/Volume7/7.2b.10N.Tucker.pdf

[1] Doshi, J. and Reneker, D. H. Electrospinning process and applications of electrospun fibers. Journal of Electrostatics. 1995, 35, 151-60

Friday 6 December 2013

(invited) 3D printing using melt electrospinning

P Dalton

Queensland University of Technology, Australia

The production of nanoscale structures has been a key aspect of electrospinning over the past decade. Following this goal, the instabilities often observed with an electrified jet have been accepted as part of electrospinning, even though the accurate placement of fibres is difficult to achieve. Conversely, additive manufacturing requires the accurate placement of objects into a three dimensional (3D) structure. Shortfalls within each technology, though, could be solved by overlapping each concept to produce new materials [1]. This lecture will describe and a distinct class of 3D printing/electrospinning that is particularly applicable for biomedical applications. This technology – melt electrospinning writing – is filling the unmet need of lower resolution fabrication limits for 3D printing while opening new areas of research for electrospinning.

Melt electrospinning writing is performed using a custom-built device that deposits electrified molten polymer jets onto a translating collector - either an x-y flat stage or a rotating cylinder. Using poly(caprolactone) as the polymer, stages were translated at varying speeds. Upon reaching a critical translation speed, the collected fibres are straight and had diameters between 1 and 200 µm, depending on the flow rate. The flow rate of the polymer to the spinneret also affected this critical translation speed, with smaller flow rates producing smaller diameter fibres which required a fast stage translation to produce a straight filament [2]. For any set of conditions, an optimum voltage (between 7 and 10kV) was required to collect a consistent diameter fibre. Figure 1 shows an electron micrograph and photograph of scaffolds fabricated using a series of 90 degree turns for the stage.

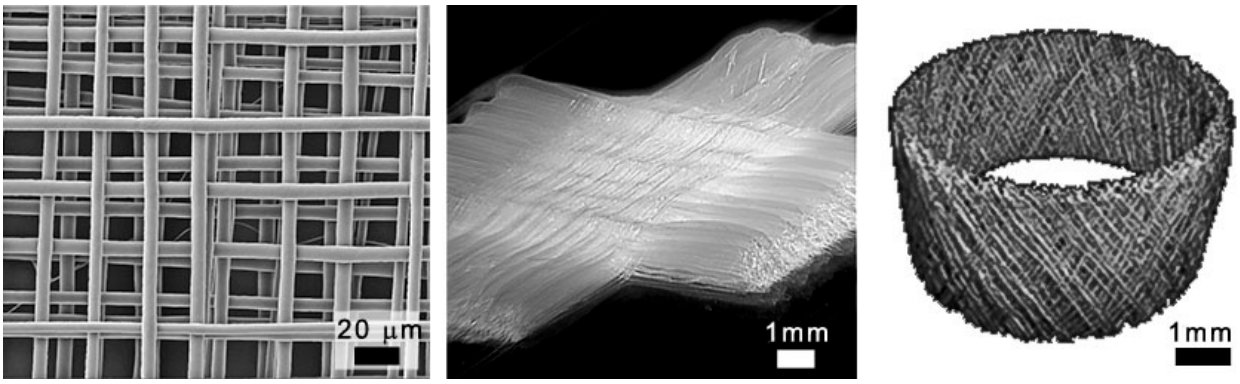

Figure 1: Cell Invasive Scaffolds produced by Melt Electrospinning Writing

The 3D printed PCL scaffolds have porosities between 87 and 95%, and are readily penetrated by cells with high survival rates [3]. The 3D printing of molten polymeric filaments is greatly enhanced by using electrostatic forces to control deposition and attain a low fibre diameter. We envision that this process will be applied to a range of polymers and used in diverse medical applications in the near future.

[1] P.D. Dalton, C. Vaquette, B. Farrugia, T.R. Dargaville, T.D. Brown, D.W. Hutmacher. Biomaterials Science, 1, 171 (2013).
[2] T.D.Brown, P.D. Dalton, D.W.Hutmacher. Advanced Materials, 23, 5651 (2011).
[3] B. Farrugia, T.D. Brown, D.W. Hutmacher, Z. Upton, P.D. Dalton, T.R. Dargaville. Biofabrication, 5, 025001 (2013).

Melt ES & TE (parallel session)

Highly aligned electrospun platforms for skeletal muscle differentiation

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[1]Institute of Composite and Biomedical Materials and DSCTM/CNR, Italy, [2]IRBM Science Park Spa, Italy, [3] Institute of Genetics and Biophysics –CNR, Italy

Tissue engineered skeletal muscle has tremendous potential for the treatment of muscular injury or muscular dysfunction (e.g. muscular dystrophy). However, in vitro methods to generate skeletal muscle with physiologically aligned myofiber structure remains limited due to the complexity of the structural organization of skeletal muscle which is naturally assembled in aligned bundles of fibers by the fusion of myoblasts into multi-nucleated myotubes. In order to mimic the highly organized structure of skeletal muscle in vitro, a promising approach consists to create oriented myofibers by the culture of skeletal myoblasts on polymer microfibers that form parallel arrays. Here, we propose the design of aligned fibres made of Polycaprolactone (PCL) and Gelatin, by electrospinning technique for a guided in vitro regeneration of muscoskeletal tissue.

Materials and Methods
PCL and PCL/Gelatin fibers were randomly collected over a grounded aluminium foil target to obtain flat membranes and onto a rotating wheel to produce aligned fibres starting from different polymer solutions (i.e. PCL/Chloroform 0,33g/ml and PCL/Gelatin/HFP 0,1 g/ml). Case by case, process parameters were optimized to obtain the best fibre morphology. Fibrous platforms were examined by SEM providing a complete detail on size and shape of the fibres and defects (i.e. beads, branched fibres). Furthermore, image analysis techniques supported by a self-made Matlab routines were used to collect quantitative information on fibre alignment and angular distribution. As an in vitro model of skeletal muscle differentiation, murine C2C12 cells (primary myoblasts) were

grown in DMEM plus 10% FBS or in differentiation medium (DMEM plus 2% HS) in a humidified incubator (37°C, 5% CO_2). Muscle differentiation was assessed by immunostaining of myoblast nuclei (DAPI) and Myosin Heavy Chain (MHC).

Results and Discussion

Highly aligned PCL and PCL/Gelatin fibres have been reproducibly made by optimizing the rotating conditions. Higher rates (3000 rpm) confer a narrow diameters distribution to fibres. The integration of Gelatin in PCL fibres determines a reduction of average fibers diameter to 0,71 ± 0,15 µm, respect to micrometric PCL fibers (3,05 ± 0,73µm). We demonstrate that the highly alignment of fibres offers a strong topographical cue which promote the alignment of C2C12 murine myotubes along a preferential way. In this study, SEM and fluorescence imaging clearly show that the cells align along the parallel axis of the electrospun fibres. In particular, fluorescence staining for the F-actin component of the cytoskeleton shows that C2C12 myoblast cells preferentially adhered onto PCL fibres. Meanwhile, Gelatin negatively influences the interaction of C2C12, probably due to both contribution of mesh size and stiffness of fibres which partially hinder its bioactive potential.

Polysaccharide based nanofibres containing curcumin for antibacterial dressing

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Production of biodegradable nanofibres from natural polymers by electrospinning has been widely studied for biomedical application such as tissue engineering or wound dressing. Among these natural polymers, polysaccharides are highly interesting. However the rigidity of the polymer chain in aqueous solutions make them difficult to electrospin. They have to be electrospun in the presence of a template polymer such as poly(ethylene oxide). Finally, because of their solubility in water, a post electrospinning crosslinking is necessary to make them stable for biomedical applications.

We present the preparation of carboxymethylcellulose (CMC)/ chitosan (Chi) core-shell nanofibres by electrospinning for antibacterial wound dressing. The use of an anionic and a cationic polysaccharide leads to the formation of an electrostatic complex that makes the nanofibres usable without crosslinking. Moreover, the addition of curcumin, a natural antibacterial agent, into the electrospinning solutions, makes them good candidates for antibacterial wound dressing.

Electrospun nanofibers applied for tissue engineering and medical therapies

T Kowalczyk[1], P Nakielski[1], M Frontczak-Baniewicz[2], D A Gołąbek-Sulejczak[2], J Andrychowski[2,3], J Adamowicz[4], T Drewa[4] and T A Kowalewski[1]

[1]IPPT PAN Warsaw, Poland, [2] IMDiK PAN, Warsaw, Poland, [3]WUM, Warsaw, Poland, [4] Nicolaus Copernicus University, CM, Bydgoszcz, Poland

Electrospinning is a cheap, convenient and fast method of nanomaterials production. It allows obtaining membranes of nanofibres similar to Extracellular Collagen Matrix. Biodegradable nanofibres can be used to form “soft” scaffold for cells culturing. Versatility of electrospinning allows forming nanofibres as pH [1] or temperature sensors, to encapsulate drugs or even living cells. Scaffolds made of proteins are treated by cells as native material. Tests conducted on mice showed that it can be used as burn dressings, protection against liaisons or to hold skin implants. Human Mesenchymal Stem Cells (MSC) cultured on electrospun nanofibers to be used for cartilage regeneration. Electrospun nanofibers covered ceramic bone implants to help osteoblasts adhesion and growth. We used model living cells to form tissue-mimicking structure for regenerative medicine. We applied flat multi-layered membranes made of electrospun nanofibers for reconstruction of urinary bladder wall and tube shaped constructs

of electrospun nanofibers for ureter reconstruction [2]. In both of this urology applications animal model studies showed superiority of nanomaterial over decellularized collagen matrix. Nanofibers were colonized by cells and material structure protected cells against a toxic urine environment. We used electrospun nanofibrous mats to protect tissue of central nervous system against excessive cicatrization in an animal model of spinal cord surgery [3]. The material served as insulation between different tissues. Nanofibers gradually degraded thus caused no foreign body reaction. Collagen fibers replaced resorbed nanomaterial. Application of nanomaterial as internal wound dressing in brain surgeries on animal model resulted in forming less reactive and more ordered glial scar. Material also acted as neuroprotecting wound dressing. We evaluated drug delivery systems based on electrospun nanofibers mats. Nanofibrous mats delivered drugs like: alpha-tocopherol, sodium glutamate, Neural Growth Factor (NGF) and Brain Derived Neurotropic Factor (BNDF). We found release profiles of the substances capped in the nanofibers in conditions simulating the subarachnoid space.

The support of NCBiR grant no 13008110 is acknowledged.

[1] Kowalczyk T., Nowicka A., Elbaum D., Kowalewski T. A. (2008), *Electrospinning of Bovine Serum Albumin.Optimization and the use for production of biosensors*, Biomacromolecules 9, pp. 2087-2090, 2008.

[2] Klosowski T., Kowalczyk T., Nowacki M., Drewa T., *Tissue engineering and ureter regeneration, is it possible?* Int J Artif Organs 36(6):392-405, 2013

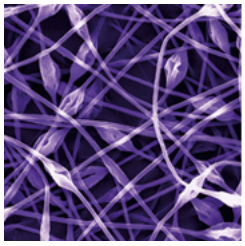
[3] Andrychowski J., Frontczak-Baniewicz M., Sulejczak D., Kowalczyk T., Chmielewski T., Czernicki Z., Kowalewski T.A., *Nanofiber nets in prevention of cicatrisation in spinal procedures. Experimental study*, Folia Neuropathologica 51, 147-157, 2013

Electrospun core-sheath PEO/Eudragit S100 nanofibers for enhanced magnetic resonance imaging

M Jin[1], G R Williams[1], S W A Bligh[2] and D G Yu[3]

[1]UCL School of Pharmacy, UK, [2]University of Westminster, UK, [3]University of Shanghai for Science and Technology, China

Magnetic resonance imaging (MRI), is a medical diagnostic tool used for detecting abnormal organs and tissues, often using Gd(III) complexes as contrast-enhancing agents. Polymer nanofibers have been prepared using coaxial electrospinning, with the intent of delivering Gd-DTPA (gadolinium(III) diethylene triamine pentaacetate hydrate) to specific tissues. Experiments were performed to make composite fibers with Eudragit S100 and Gd-DTPA-loaded PEO (polyethylene oxide) as the sheath and core matrix respectively. The systems were studied using scanning and transmission electron microscopies (Fig. 1), differential scanning calorimetry and X-ray diffraction. The Gd-DTPA-loaded PEO/Eudragit S100 fibers were found to be homogeneous with average diameters of 272 ± 73.2 nm, and to have distinct core/sheath phases (Fig. 2). The components in the fibers were dispersed in an amorphous fashion. The fibers were also studied using Fourier transform infrared spectroscopy, which indicated good compatibility between the Gd complex and polymers. *In vitro* dissolution tests showed that nanofibers coated with Eudragit S100 did not exhibit any release in acidic solution (pH 1), but sustained release at pH 6.8. This simple and straightforward approach thus offers a new technique for the design and fabrication of nanofibers to release Gd-DTPA to the colon-targeting.



Electrospinning, Principles, Possibilities and Practice 2013

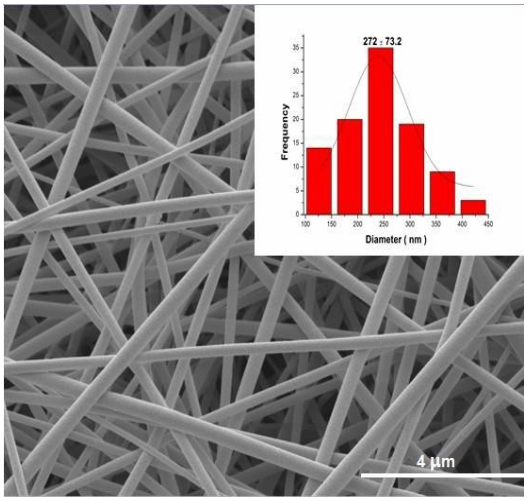


Figure 1. SEM image of Gd-DTPA-loaded PEO/Eudragit S 100 fibers and the fibers

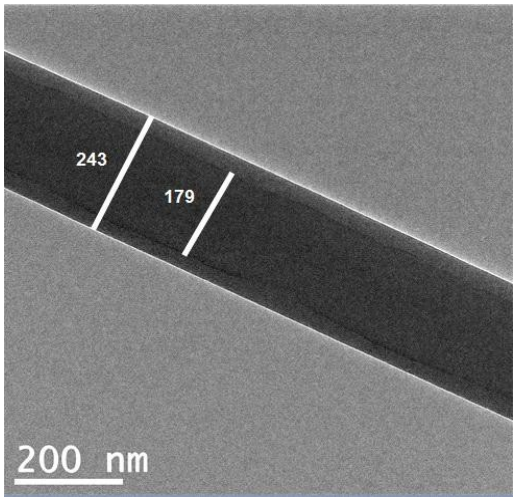


Figure 2. TEM image showing core/sheath structure the size distribution of

Electrospun, cross-linked poly(aspartic acid) based fiber matrix: preparation and biological application

K Molnár, L Rago, O S Bata, M Czobel, A Jedlovszky-Hajdu, Gy Weber and M Zrinyi

Semmelweis University, Hungary

The importance of nanotechnology is well recognized in the area of biomedical applications. The interest in the development of biocompatible and biodegradable polymer matrices has increased with their usability in wide range. In many biological applications, such as tissue engineering, there is a desire for well-defined 3D scaffolds with high surface area for cell attachment and growth. The use of electrospinning enables the possibility to prepare such tailored mashes, however the use of water soluble polymers is inappropriate because of their fast dissolution in biological fluids. To prevent dissolution one can introduce cross-links to the polymer chains creating the fibrous meshes. By utilizing reactive electrospinning technique, the desired cross-linked system can be obtained which will not dissolve without chemical or enzymatic degradation inside the body.

Poly(amino acid)-based polymers that have desirable chemical, mechanical and biological properties have recently emerged as promising new class of biomaterials [1-2]. In our work we have utilized the anhydrous form of poly(aspartic acid), the poly(succinimide) as base polymer. In order to imitate the structure of the backbone of the connective tissue, electro-spinning technique was applied to prepare artificial extracellular matrix. To prevent the polymer fibers from dissolution poly(succinimide) molecules were grafted by thiol side chains During the electro-spinning process at 10 kV (0.8 ml/h flow rate and 15 cm target distance) cross-linking reaction took place between the side chains. The mean value and distribution of the fibre diameter were determined with AFM and light microscope after the sample preparation [3]. *In vitro* biocompatibility test with human fibrosarcoma (HT1080) and human fibroblast cells was performed. It was followed by *in vivo* experiments on albino rabbits. We have found that cross- linked poly(aspartic acid) based fiber matrix degraded and disappeared within eleven days. Our novel biocompatible and biodegradable artificial scaffold seems to be a promising poly(amino acid) based fiber matrix for tissue replacement.

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Development of bio-compatible polymer films via electrospinning for use as synthetic membranes to cure retinal degeneration

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University of Southampton, UK

Age-related macular degeneration (AMD) is the leading cause of blindness in those over 65 years of age in the developed world. There is currently no treatment available to cure the progressive degeneration of photoreceptor cells caused by AMD, leading to the loss of central vision.

Injection of RPE cells under the retina has been suggested as a potential therapy to support photoreceptor cell function; however this leads to issues associated with lack of organisation & movements of cells away from the injection site. Here we show a potential solution to these problems through the development of a bio-compatible polymer film via the use of electrospinning, designed to mimic the natural Bruch's membrane (BrM) and to allow RPE cells to attach to the surface and proliferate.

This work demonstrates the synthesis of a PMMA:PEGM co-polymer film, through the use of the electrospinning technique. This co-polymer film mimics the necessary properties of the BrM, such as porosity, thickness, biocompatibility & adhesion, and can therefore provide a viable scaffold for RPE cells to adhere and proliferate from, and to be delivered into the sub-retinal space of the eye.

Applications (parallel session)

Electrospinning research at Rhodes University

S Chigome and N Torto

Rhodes University, South Africa

Our primary research focuses on the development of electrospun nanofiber based devices for analytical chemistry applications [1-2]. Recently, our electrospinning activities have expanded to cover other areas like energy [3] and advanced surfaces among other areas. The presentation will give an overview of the developments in electrospinning research at Rhodes University over the period 2009 to 2013.

The first section of the presentation will focus on our use of electrospun nanofibers in analytical device fabrication for sample preparation [2,4-6], high resolution separation and detection. In the second section, we will present our work on the development of electrospun carbon nanofiber based electrodes for microbial fuel cells [3]. Lastly, we will present our efforts towards the development of electric field assisted rapid expansion of supercritical carbon dioxide set-ups for controlled deposition of superhydrophobic surfaces.

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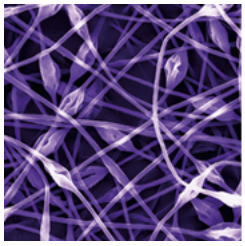

Electrospinning, Principles, Possibilities and Practice 2013

Influence of temperature on the photodegradation process using Ag-doped TiO_2nanostructures: Negative impact with the nanofibers

N A M Barakata[2], M A Kanjwal[3], I S Chronakis[3] and H Y Kim[1],

[1]Chonbuk National University, Republic of Korea, [2]Minia University, Egypt, [3]Technical University of Denmark, Denmark

In this study, the influence of the temperature on the photodegradation process using Ag-doped TiO_2 nanostructures was investigated. Two morphologies were used; nanoparticles and nanofibers. The nanofibers were synthesized by electrospinning of a sol–gel consisting of titanium isopropoxide, silver nitrate and poly(vinyl acetate). The silver nitrate amount was changed to produce nanofibers having different silver contents. Typically, sol–gels containing 0.5, 1.0, 1.5, 2.0 and 2.5 wt% silver nitrate were utilized. Calcination of the electrospun mats at 700 ˚C led to produce well morphology Ag-doped TiO_2 nanofibers for all formulations. The nanoparticles were prepared from the same sol–gels, however, instead of spinning the gels were dried, grinded and sintered at 700 ˚C. Photodegradation under UV irradiation for the rhodamine B at 5, 15, 25, 45 and 55 ˚C were performed. For the nanoparticles, increasing the temperature has positive impact as the best degradation was obtained at 55 ˚C. In contrast to the known influence of the temperature on the chemical reactions, in case of the nanofibrous morphology, the temperature has negative impact as the experimental work indicated that the optimum temperature is 25 ˚C. The observed strange effect of the temperature in case of the nanofibrous morphology indicates instant degradation of the dye molecules in the active zones surrounding the nanofibers. Therefore, the increase of temperature results in increase the kinetic energy of the dye molecules so the molecules escape from the active thin film surrounding the photocatalyst. Overall, this study shows that the nanofibrous morphology strongly enhances the surface activity of the photocatalyst which generates negative influence of the temperature.

Applications of electrospinning of biopolymers in the food and food packaging areas

J M Lagaron

IATA, CSIC, Spain

Looking genuinely at nature, nanofibers often serve as a basic platform where either organic or inorganic components are built upon. For instance, cellulose nanofibers would represent the building block in plants while collagen nanofibers in the animal body. The fiber structure exhibits, from a structural view point, the ability to transmit forces along its length and generate barrier properties against the transport of low molecular weight components. To follow this extraordinary nature's design, technologies able to fabricate nanostructured fibers from a variety of materials and mixtures is an indispensable pre-requisite. Control over the nanofibers arrangement, size, composition and morphology is also necessary to optimize such structural requirements.

Electrospinning is a physical process used for the formation of ultrathin fibers by subjecting a polymer solution to high electric fields. At a critical high voltage (5-35 kV), the polymer solution droplets distort and forms the so-called cone of Taylor that erupts from the solution to form a charged polymer jet. This stretches and is accelerated by the electrical field towards a grounded and oppositely-charged collector. As the electrospun jet travels through the electrical field, the solvent completely evaporates while the entanglements of the polymer chains prevent it from breaking up. This results in the generation of highly functional and flexible ultrathin polymer fibers in the form of non-woven mats. In this area, our group have recently developed high throughput equipment based in a multinozzle coaxial technology that allows high productivity of fibers.

The current paper will present innovative advances carried out within our research group in which various applications of the high voltage spinning processing technique making use of biopolymers and biopolymeric blends will be reviewed (1-10). These include examples in which new antimicrobial nanostructured fiber mats with strong biocide efficiency were successfully developed, as well as nanoencapsulates of active and bioactive food

ingredients, nanostructured temperature buffers with heat storage capacity and high barrier nanobiocomposites and nanolayers of interest in food packaging applications.

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Biological (parallel session)

Bioactive electrospun fish sarcoplasmic proteins as a new oral delivery system

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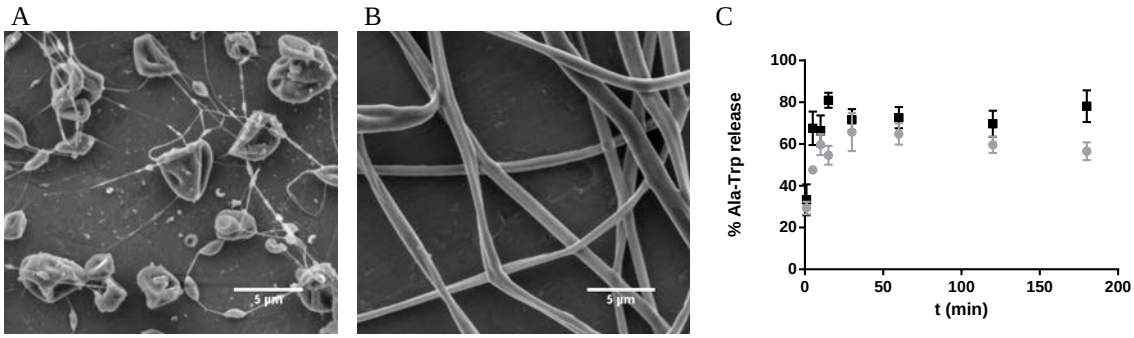
Technical University of Denmark, Denmark

As a natural protein source for electrospinning, fish proteins are very attractive. The fish muscle contains all the essential amino acids, and may be regarded as a complete protein source. Additionally, fish protein hydrolysates have been shown to contain bioactive properties. Protein based systems have previous been electrospun, however in most cases, a thorough post treatment with various toxic agents are needed, to obtain desired properties of the fibers (*e.g.* crosslinking to obtain insoluble fibers).

In this study we present naturally occurring, water soluble, cod (*Gadus morhua*) sarcoplasmic proteins (FSP) (Mw < 200 kDa) electrospun into insoluble nano-micro fibers, without the need of a carrier system or other additives. When exposed to proteases, the fibers were degraded directly into small peptides, rather than in large fragments. The degradation products proved to be inhibitors of the diabetes related enzyme DPP-IV, giving the FSP fibers an inherent bioactivity.

To illustrate how FSP fibers may be used as a delivery system, a dipeptide (Ala-Trp) was encapsulated into the FSP fibers. The release profile of Ala-Trp from FSP-(Ala-Trp) fibers, showed a maximum release (~70 %) within 30 min (solvent at pH 1.2) or 15 min (solvent at pH 6.8). The remaining 30 % of the Ala-Trp was not released unless the fibers were enzymatically degraded.

Moreover, due to the unique properties of the fibers (*e.g.* water insoluble, biodegradable, and bioactive) they may also find applications in tissue engineering – which is a current focus in the group.



A and B: SEM images of electrospun FSP, scale bar: 5 µm. The figures show how fiber morphology depends on FSP concentration. A: [FSP] = 50 mg/ml, B: [FSP] = 125 mg/ml. C: Ala-Trp release from FSP-(Ala-Trp) fibers in solvent at pH 1.2 (●) and solvent at pH 6.8 (■)

Ref.: Stephansen, KB., Chronakis, IS., Jessen, F, *Bioactive Electrospun Fish Sarcoplasmic Proteins as a New Oral Delivery System*, submitted.

Functional nanofibers based on natural polymers

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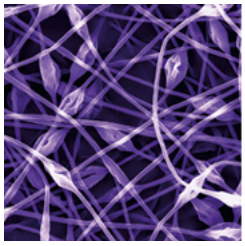
Istituto Italiano di Tecnologia, Italy

Nanofibers based on biopolymers derived from natural sources, such as chitosan, silk, alginate, and cellulose, are of interest for the production of filters, membranes, smart fabrics, nanocomposites, tissue engineering scaffolds, drug delivery and wound dressing systems. In fact, together with the related functional properties, the use of biopolymers offers remarkable advantages in terms of biocompatibility, biodegradability and environmentally friendliness. Here, we present the realization of composite nanofibers in polysaccharides functionalized with different active agents.

As materials of interest we focused our attention on sodium alginate, a polysaccharide extracted from brown algae where it works as biosorbent of metals. We demonstrated the realization of ultrafine alginate fibers (diameter of about 50 nm) encapsulating a gold precursor, and we used them as chemical reactor for the *in-situ* synthesis of gold nanoparticles. The obtained bionanocomposite fibers have potential applications in biosensors, immunoassays and biochemical analysis.

Moreover, we realized cellulose electrospun nanofibers with unique chemical and wetting properties by choosing the right combination of chemical agents and biopolymer. Natural antimicrobial compounds, in particular essential oils, were incorporated within the nanofibers in order to obtain controlled release of functional molecules. The fibers were characterized by antiseptic activity and they are effective against Escherichia Coli and Candida Albicans. These composite fibrous scaffolds are attractive for textile applications, filtration and active packaging.



Tailoring electroactive response of poly(vinylidene fluoride) electrospun membranes for tissue engineering applications

V Sencadas[1,2], C Ribeiro[1] and S Lanceros-Mendez[1]

[1]Centro/Departamento de Física, Portugal, [2]Instituto Politécnico do Cávado e do Ave, Portugal

Scaffolds used in tissue engineering are designed to mimic human body properties in order to match structural, morphological, mechanical and chemical properties of the tissue or organ that will be replaced. Apart from blood, most, if not all, human cells in human tissues are anchorage dependent residing in a solid extracellular matrix that depends on the tissue in analysis [1]. Cell/biomaterial compatibility and cell response are deeply influenced by material surface characteristics such as chemical composition, roughness and surface charge content and distribution, among others. In particular surface charge and therefore electric field have been proven to influence cell attachment and growth of specific cell types.

This presentation will focus on the main properties of the electrospun membranes for tissue engineering applications as well as on the electrospinning processing strategies to obtain them. In particular, the effect of the processing parameters on fiber morphology and orientation and on the degree of crystallinity and crystal phase produced will be presented and several examples discussed. Further, the influence of piezoelectric stimulus under static and dynamic conditions on the response of MC3T3-E1 osteoblast cells will be evaluated.

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In vivo response of bicomponent electrospun conduits for peripheral nerve regeneration

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[1]Institute of Composite and Biomedical Materials and DSCTM/CNR, Italy, [2]New Jersey Center for Biomaterials, USA

A number of criteria for the ideal nerve conduit can be outlined, including: limiting scar infiltration, while allowing diffusion of nutrients into the conduit and wastes to exit the conduit; providing sufficient mechanical properties for structural support; exhibiting low immune response; biodegradability, to remove the need of a second surgery and to prevent chronic inflammation. Here we developed micro and nanostructured fibrous conduits to bridge critical nerve gaps and promote neural regeneration, as alternative strategy to the autologous graft.

Materials and Methods

Electrospun fibres were obtained by using an automatic equipment (Nanon01, MECC, Japan). Different polymer solutions (i.e. PCL/Chloroform 0,33g/ml and PCL/Gelatin/HFP 0,1 g/ml) were processed. Fibers were randomly collected over an aluminium foil target to obtain flat membranes and onto a 1,5 mm diameter rotating mandrel to produce nerve conduits. A qualitative evaluation of the electrospun PCL and PCL/Gelatin membranes/tubes was performed by scanning electron microscopy (SEM). Tensile test on electrospun membranes and transverse compression testing of tubes were performed by using a dynamometric machine (Instron 5566). Biological validation *in vitro* with Dorsal Root Ganglia (DRGs) was made on flat membranes while conduits were compared *in vivo* when implanted in the 5 mm rat sciatic nerve defect in an 18-week study.

Results and Discussion

The addition of Gelatin in PCL solution assures a reduction of fibers average diameter to 0.59 ± 0.15 μm, respect to micrometric PCL fibers (5.61 ± 0.80 μm). The smaller network size scale and consequently the higher scaffold surface area, fibers can interact more effectively with cells *in vitro*. Unfortunately, the Gelatin addition also affected the stiffness of conduits. Therefore, animals implanted with PCL conduits had better recovery of the injured muscle weight and electrophysiological signal, as well as more mature nerve morphology, as seen from histologies, compared to PCL/Gelatin conduits.

Conclusion
PCL and PCL/Gelatin solutions were successfully processed. Despite the positive effect of Gelatin integration on the characteristic network size scale and on the interaction with cells *in vitro* PCL electrospun conduit appears to be the more promising device to support the *in vivo* regeneration of peripheral nerve.

S & P & Applications

(invited) Nanofibres and nanoparticulates

F Davis

University of Reading, UK

In this presentation we shall look at the way in which particulates can be incorporated into electrospun fibres. The modification of material properties by the formation of composites is an important route to the development of materials with new or tailored properties. Thus additives may introduce properties such as conductivity or high strength. For polymers this may involve, for example, suspending materials in the polymer matrix.[1] Electrospinning generates nano and micro-scale polymer fibres as a consequence of applying a modest electric field (~1kV/cm) to droplets of a polymer solution, typically emerging from a the needle of a syringe system.[2] Thus any consideration of the production of such composite materials needs to consider the dimensions of the fibres.

The simplest approach to the problem producing fibres of an intractable material is to suspend particles of the material in a solution containing a carrier polymer. The carrier polymer concentration required will depend on the particles but can be relatively low in terms of the total mass of material. Crucial to this is that the dimensions of the particulates do not exceed those of the fibres produced. Otherwise there may be swelling of the fibre or indeed material ejected. as shown by Figure 1 which shows a sample of polyethylene oxide containing microfibrillated cellulose material. For intractable materials thus we need to consider the particle size. For example conducting polypyrrole materials can be manufactured with dimensions lower than a few hundred microns (Figure 2); with suitable control these particles may be electrospun. In addition to size it is important the particles do not merge together, or they will precipitate from solution (and may also become too large to spin). A number of systems will be discussed and routes to controlling the properties of the resulting composite fibres will be described.

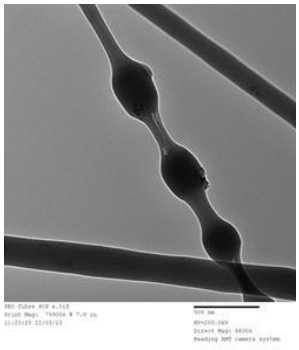

Figure 1: Electrospun polyethylene fibres containing microfibrillated cellulose

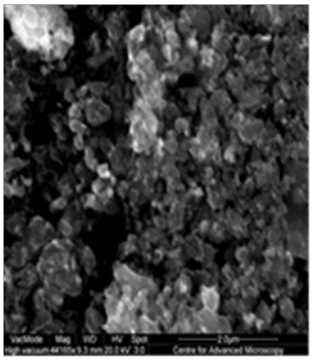

Figure 2: Polypyrrole particles prepared using an emulsion polymerisation stabilised with DTAB; the particles obtained had a good spherical morphology with sizes in the range of 100-200nm

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SANS study of chain conformation and relaxation kinetics of electrospun polystyrene fibers

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[1]Université Joseph Fourier, France, [2]Genie et Microbiologie des Procedes Alimentaires, INRA, France

Electrospun nano-structured scaffolds represent an advantageous material for tissue engineering in terms of cost, high porosity, lightness, and organization similar to the one in extracellular matrix (ECM). Working with biodegradable polymers for medical applications necessitates a significant knowledge about the stability of a polymer chain composing a biomaterial. Herein, we investigated the stability of electrospun fibers by studying the polymer chain conformation and relaxation dynamics after thermal annealing. Electrospun scaffolds of aligned fibers were made of amorphous polystyrene having narrow polydispersity index and further analyzed by small angle neutron scattering technique (SANS). Previous SANS studies of micron-sized electrospun fibers made of polystyrene were dealing with the polymer chain conformation in as-spun state, reporting only small signs of anisotropy of the polymer chains with the values of the radius of gyration broadly equivalent to that of the bulk state.[1] In addition, notable difficulties in data analysis and modeling have been encountered, likely due to the high porosity of the scaffold and at the surface of the fibers.[2] Herein, we report a different approach for studying the anisotropy of polymer chains within electrospun fibers. Unlike classical approaches for studying the chain conformation and radius of gyration that involve complex SANS data modeling, we obtained the characteristic size of macromolecular chains through investigation of the chain elongation ratio from experimental SANS data and iso-intensity curves. SANS experiment on polystyrene fibers in as-spun state showed a notable anisotropy of polymer chains in the direction of the fiber alignment axis. The elongation ratio in the axial direction of as-spun fibers was found to be 1.22 while the corresponding ratio of the radius of gyration parallel and perpendicular to the fiber alignment axis was 1.34. Furthermore, the chain relaxation dynamics after thermal annealing at different temperatures and time intervals were reported. Fast relaxation of the surface of electrospun fibers and rather slow chain relaxation within the fiber bulk were observed. The thermal annealing experiments enabled us to estimate the characteristic relaxation time of the polymeric chains within the electrospun fibers.

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[2] S. D. Mohan; F. J. Davis; R. H. Olley; G. R. Mitchell *Journal of Physics: Conference Series* 2010, 247, 012042

SANS study of electrospun polymer fibres

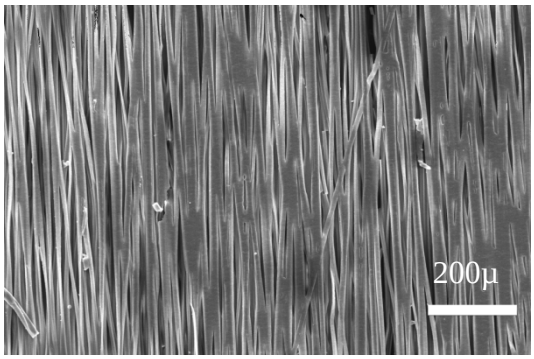
S D Mohan[1], F J Davis[1] and G R Mitchell[2]

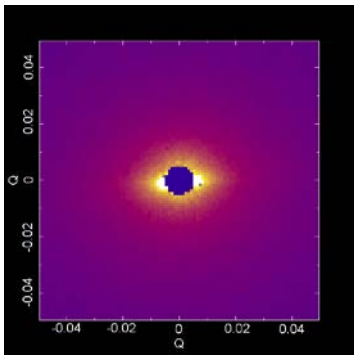
[1]University of Reading, UK, [2]Polytechnic Institute of Leiria, Portugal

Electrospinning is a technique which readily produces nanoscale to microscale sized polymer fibres from a solution or melt [1]. During this process a sub millimetre sized polymer droplet is extruded into a microscale to nanoscale sized polymer fibre in a short time frame. This can result in a large scale transformation ratio, one which Reneker estimated to be around 60,000 [2]. This large scale, rapid transformation from solution to a solid fibre may potentially impact upon the polymer chains. Understanding this process can lead to control of the bulk properties of the materials used. Here we study electrospun fibres with small angle neutron scattering (SANS), a powerful technique that can be used to measure polymer chains dimensions in the bulk or solution state through the use of isotopically substituted polymer chains [3]. A deuterated polymer has been synthesised and prepared in a 1:1 ratio with the protonated polymer in order to provide maximum possible contrast. In this case the polymer was

polystyrene and fibres were prepared from both dimethylformamide (DMF) and methyl ethyl ketone (MEK) at a variety of concentrations.

Examination of scattering patterns from isotopically labelled samples and purely deuterated fibres showed a strong scattering power from nanoscale voiding within the fibre structure as confirmed by SEM images. A model was developed that takes into account the scattering from the nanovoids combined with the polydisperse Gaussian coil model allowing for the extraction of the radius of gyration of the polymer chains within the fibres.
In order to examine the radius of gyration in solution, isotopically labelled chains were mixed in with the normal protonated chains in a deuterated solvent. This allowed us to match out the contribution to the scattering from the structure factor, thereby allowing for the radius of gyration of the polymer chains in the solution to be extracted through the use of polydisperse Gaussian coil model.
Finally we have measured the chain dimensions parallel and perpendicular to the fibre axis in order to see in if there is any potential extension of the polymer chains during this rapid, large scale transformation. We then explore further deformation of the chains through mechanical means during fibre collection through the use of rotating collector.





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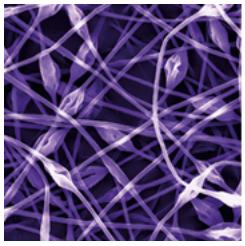
Supercapacitance from electrospun cellulose/carbon nanotube nanocomposite fibers

S J Eichhorn[1], R J Young[2], L Deng[2] I A Kinloch[2], A Abdelkader[2], S M Holmes[2] and D A De Haro-Del Rio[2]

[1] University of Exeter, UK,[2] University of Manchester, UK

Multi-walled carbon nanotube (MWNT)/cellulose composite nanofibers have been prepared by electrospinning a MWNT/cellulose acetate blend solution followed by deacetylation. These composite nanofibers were then used as precursors for carbon nanofibers (CNFs). The effect of nanotubes on the stabilization of the precursor and microstructure of the resultant CNF were investigated using thermogravimetric analysis, transmission electron microscopy and Raman spectroscopy. It is demonstrated that the incorporated MWNTs reduce the activation energy of the oxidative stabilization of cellulose nanofibers from 228 to 203 kJ mol^{-1}. They also increase the crystallite size, structural order and the electrical conductivity of the CNFs. The surface area of the CNFs increased upon addition of nanotubes which protrude the fiber surface leading to a rougher surface. The CNFs were used as the electrodes of supercapacitor. The electrochemical capacitance of the CNF derived from pure cellulose nanofiber is demonstrated to be ~120 F g^{-1} at a current density of 2 A g^{-1} which increases to ~150 F g^{-1} upon the addition of MWNTs.



Electrospinning, Principles, Possibilities and Practice 2013

Electrospun Plus

Tough electrospun polystyrene nanocomposites

F Zhang and A H Barber

Queen Mary, University of London, UK

Fibrous materials are commonly processed into composites for structural applications. While electrospun fibres have been previously used in composites, the resultant mechanical properties are often poor and restrict their use as structural materials [1, 2]. Polystyrene (PS) is a notable example of an engineering polymer with inferior mechanical properties. However, electrospinning is able to improve both the elastic modulus and the strain to failure of PS considerably when processing the polyer as nanofibres to give a resultant structurally tough material. This work demonstrates the fabrication of nanocomposites incoporating electrospun PS nanofibres for a wide range of applications, especially in transport systems where the large energy absorbed by the lightweight composite material is considered particularly advantageous in impact. Experimental results are compared to potential theoretical limits to highlight the potential of polystyrene nanocomposites as a novel impact resistant material that is able to outperform current engineered composites.

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Controlling the pore size of 3D electrospun biomaterials using simultaneously and synergistically electrospinning, electrospraying and architectured collectors

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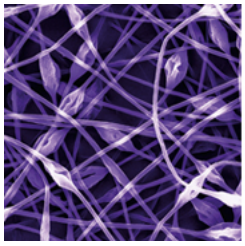
In the last decade, electrospinning emerged as a powerful technique to design biomaterials for regenerative medicine. The ability of this technique to produce nanofibers that can mimic the extracellular matrix (ECM) makes it a technology of first order for application such as wound healing, bone regeneration, cardiac patches or vascular grafts. However, despite the high potential of those biomaterials, the small size of the pores of an electrospun fibrous mat (1 to 5 microns in average) that doesn't allow for enough cell penetration and migration stays an issue. Aiming to solve this issue, we are showing here a new generation of fibrous 3D biomaterials mimicking the ECM, possessing controlled pore size from 30 to 300 microns. It's been shown that under peculiar conditions, bimodal fibers with thick (beaded shape) and thin domains having different transient electric properties can be formed[1]. Under these conditions, fiber self-assembly into honeycomb patterns occurs, leading to the building of thick scaffolds with pores of an average size of 10-100 microns. Recently we demonstrated that regular thin nanofibers can also form these kind of scaffolds if microparticles (playing the role of the thick domains) are electrosprayed simultaneously with the electrospinning.[2] In parallel, we showed that structured electrospun 2D scaffolds can be fabricated with the help of micropatterned collectors.[3] We decided here to combine both techniques. Thus, uniform electrospun fibers and electrosprayed microparticles were simultaneously deposited onto micropatterned collectors . We'll show here how the size of the fibers, concentration of the spheres and size of the patterns interplay to build well controlled 3D fibrous and porous materials. Finally, beyond the fact that those materials made of biocompatible polymers have the potential to become excellent scaffolds for tissue engineering, we also believe that this strategy opens the way for other applications that can be improved by the use of composite self-assembled materials having fibers and beads made of different materials.



Electrospinning, Principles, Possibilities and Practice 2013

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[2] Nicolas Lavielle, Anne Hébraud, Guy Schlatter, Linda Thöny-Meyer, René M. Rossi, Ana-Maria Popa, "Simultaneous electrospinning and electrospraying: a straightforward approach for fabricating hierarchically structured composite membranes", web on line, *ACS Applied Materials and Interfaces*, DOI: 10.1021/am402676m, 2013.

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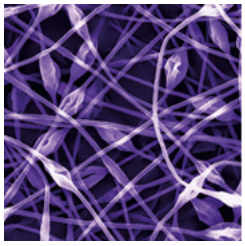

Electrospinning, Principles, Possibilities and Practice 2013

Poster Abstracts

P.01 Enhancing the optical properties of silicon quantum dots using silver nanoparticles

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There is a growing interest in the applications of noble metal nanoparticles (NPs) in optics and electronics due to their unique optical properties. For example, metallic NPs have been used as a light scattering source in solar cells and silver nanoparticles are widely used in plasmonics applications. This study focused on the enhancement of the optical properties of silicon quantum dots (SiQDs), and their mixtures with silver nanoparticles (AgNPs). In addition, structural characterization of SiQDs was achieved via scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), atomic force microscopy (AFM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The results confirmed that the SiQDs have a polycrystalline and amorphous structures with an average particle size diameter of 65 nm. The AgNPs were synthesised in two concentrations via the photolysis of silver nitrate at room temperature in sun light, using sodium dodecyl sulphate (SDS) solution as an anionic surfactant. The two concentrations (1 & 10 mM) of synthesized AgNPs have a polycrystalline structure with an average particle diameter of 100 nm and 30 nm respectively. The optical properties of the SiQDs, AgNPs and their mixtures were characterized by UV-Vis spectroscopy, Surface Enhanced Raman Scattering (SERS) and confocal photoluminescence spectroscopy. A significant enhancement in silicon Raman signal was observed in the presence of AgNPs.

P.02 The effect of humidity on the electrospinning of poly(vinyl alcohol)

M Aumonier and S Coles

WMG, UK

The fibre diameter, distribution of diameters and surface morphology are important properties of electrospun fibres. This study has investigated how the ambient parameter of Relative Humidity (RH) effects the properties of poly(vinyl alcohol) (PVOH) fibres. An aqueous solution of PVOH (8% w/w) was prepared by dissolving at 95 °C for 3 hours. The solution was then electrospun at various levels of RH in intervals of 5% between 25%-95%. The fibres were spun for 1 hour with an induced voltage of 10 kV and a distance of needle to ground of 10 cm. The morphology, diameter, and structure of electrospun nanofibers were assessed by scanning electron microscopy (SEM). As the RH level increased it was observed that the average fibre diameter size decreased along with smallest level of standard deviation between the fibre diameters. Furthermore, irregular beading formed at high levels of RH indicating an unstable Taylor Cone during fibre production. The surface of the PVOH fibres appeared to be unaffected by the RH.

P.03 Electrospinning of nanofibrous materials for fuel cell applications

S Cavaliere, S Subianto, I Savych, G Ercolano, S Giancola, Y Nabil-Moreau, D J Jones and J Rozière

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Proton exchange membrane fuel cells (PEMFC) have received significant research attention due to their potential as a sustainable source of energy for portable and stationary applications. Nevertheless, many

challenges remain in improving the efficiency and lowering the cost of the involved materials, which have lead to increased attention not only to their nature but also to their micro and nanostructure.

In this regard, electrospinning is a promising technique in the synthesis of nanofibres with controlled and uniform diameters and structures. Its versatility allows the production of organic as well as hybrid and inorganic nanofibres, extending their use from polymer electrolytes to electrode materials. Furthermore, the possibility of creating different geometries, assemblies and architectures greatly increases the range and variety of materials that can be achieved. In our group, we are developing fuel cell core materials based on electrospun fibres, due to the beneficial effect of the 1D structure on stability and performance[1].

On the one hand, we work on proton exchange membranes based on interconnected fibres of electrospun ionomers (Fig. 1a). Promising results in terms of ionic conductivity and mechanical resistance using long and short side chain PFSA were obtained[2]. The possibility of forming composite membranes using different polymers and also inorganic fibres as a reinforcement is also exploited.

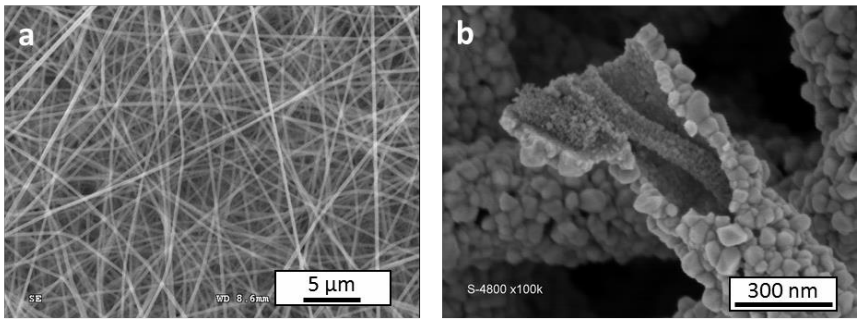

Figure 1. PFSA fibres (a) and Nb doped SnO2 loose-tubes obtained by electrospinning.

On the other hand, we are developing novel nanofibre based PEMFC electrodes. As catalyst supports, we use carbon but also metal oxides such as TiO_2 and SnO_2 previously doped with heteroatoms to increase their electrical conductivity (Fig. 1b). The latter represent a very attractive alternative to conventional supports because of their (electro)chemical stability and promoting effects, leading to improvements on the catalytic activity and stability of fuel cell catalysts[3,4.]

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[4] S. Cavaliere, S. Subianto, I. Savych, M. Tillard, D.J. Jones, J. Rozière, *J. Phys. Chem. C* 2013, 117, 18298-18307.

P.04 Multifunctional nanocomposites: The use of filled electropun fibers as functional modifier

G Cicala, A Latteri, G Ognibene, S Mannino, G Cozzo and A Recca

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The present work is focused on the development of novel multifunctional composites based on the use of hierarchical structures. The concept studied herein is the use of soluble thermoplastic fibers to add functionalities in selected positions of a composite laminates. The use of soluble fibers (both melt extruded and electrospun) as toughening aids for liquid molding technologies was reported [1-4]. Among these studies only few dealt with the use

filled fibers to modify the laminates [5,6]. However, no study, to the best of our knowledge, proposed to use soluble fibers as a carrier for nanofiller to add functionalities in selected layers of the composite laminates. The objective of the paper is to offer a proof of concept of the proposed approach and to unveil the driving parameters of the dissolution process.

Results and discussion

Different epoxies monomers were used in the present study varying from difunctional (DGEBA) and trifunctional (TGAP) resins. Electrospun fibers based on polyethersulphone were manufactured with different content of nanofillers. The fiber's dissolution was studied in a first instance by the use of hot stage microscopy. Figure 1 show the dissolution time for two different thermoplastics (PES with low molar mass (PESlow) and PES with higher molar mass (Gafone)) and fibers filled with 0.1 and 1wt% of MWCNT. Laminates were manufactured with resin infusion interposing 5 and 10 layers of electrospun PES fibers between two layers of non-crimp glass fabrics. The presence of voids helped to reveal the dissolution of the filled fibers well wet by the resin in contrast to fiber that were not wetted by the resin. DMA testing were also used to test the effect of fiber and filler addition. The results showed strong effects of the thermoplastic leading to phase separation. The nanofillers lead to higher damping.

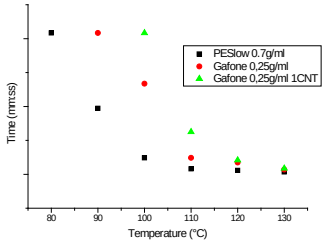

Fig 1 Dissolution time for some PES fibers in DGEBA/MDEA resin

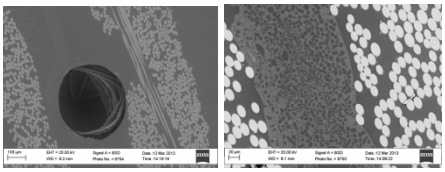

Fig 2 SEM images of the laminates with PES membrane filled with MWCNT

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[6] Gang Li et al. Materials Chemistry and Physics (2012), Vol.134, pp.958-965.

P.05 In vitro investigation of human cell viability, proliferation and migration on a biodegradable 3D-electrospun scaffold

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University of Tulsa, USA

The aim of this work is to develop physiologically relevant biodegradable 3D model systems by electrospinning for use in tissue engineering and in vitro toxicology. The effect of scaffold morphological architecture on human cell growth efficiency has not been investigated in depth. Fabrication methods greatly influence cell viability, signaling,

and differentiation of seeded cells. In addition, the biomaterial must be characterized and its physical properties must be determined having current industry and environmental consideration. Scaffolds require controlled porosity, interconnected networks, and mechanical integrity in order to serve as suitable substrates for tissue engineering. Solid freeform fabrication (SFF) methods show enormous potential for the fabrication of biomedical scaffolds. Recent, electrospinning has provided an alternative low-cost production method for generating 3D scaffolds. It is the interest of this lab to design a biomedical scaffold using electrospinning methods, which can overcome the limitations of conventional fabrication methods. In this study we will present the developed scaffolds and their application as a suitable 3D substrate for the growth of adherent fibroblast cells. The biochemical and morphological relationship the cells express under various growth conditions on the distinctly designed and characterized 3D scaffolds will be described.

P.06 Metal and metal oxide electrospun nanowires for PEMFC applications

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A plethora of emerging and established mobile devices, operating on electrical energy are pushing the research and the market towards continuous sustainable and clean sources of energy. Widely spread applications, from automotive to IT and communications, would profit from the introduction of proton exchange membrane fuel cells (PEMFC). This class of fuel cell can provide clean and long lasting electrical energy while being portable and operated at relatively low temperatures.

However a reduction of the fabrication costs and an improved durability are pivotal to a successful market introduction of this technology. A more effective utilisation of the highly priced Pt catalyst and the use of more durable materials for the catalyst supports are the core of the development of novel, market ready PEMFC.

Electrospinning has been proved to be a reliable and scalable technique for the production of nanowires made of several metals [1] and metal oxides [2]. The capability to finely control the diameter and composition of the nanowires makes this technique appealing in the search of novel catalyst support materials and morphologies. Our research group is actively producing and testing different metal oxide nanowires and nanotubes, pristine and doped, as well as metallic nanowires using this facile technique.

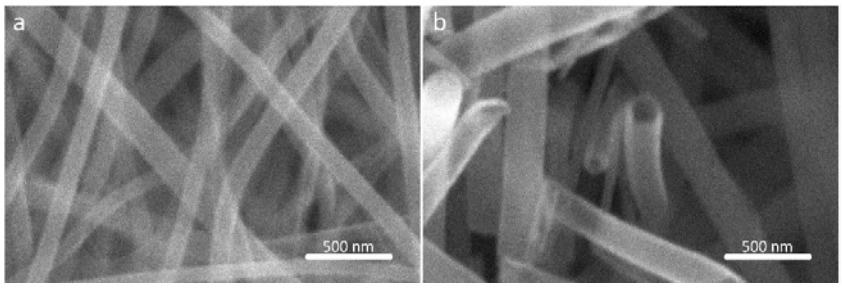

Figure 1. TiO2 nanowires (a) and TiO2 nanotubes (b) obtained by electrospinning.

Furthermore the use of electrospun metal and metal oxide supports allows novel, alternative platinum deposition techniques to be exploited. A paradigm shift from Pt nanoparticles supported on carbon to atomic layers of platinum deposited on metals or metal oxides can be achieved coupling the electrospinning to electrochemical Pt deposition techniques like the galvanostatic displacement of Ni and Cu ions with Pt [3] or the self-terminated Pt electrodeposition [4]. This novel morphology could push the boundary of Pt exploitation further and vastly increase the stability of the electrodes, therefore the sought after reduction of fabrication costs and increased stability are within the reach of current researches.

On the other hand electrospun supports can also be utilised with Pt nanoparticles synthesised by conventional or novel routes like the microwaves assisted polyol method [5] and more directly compared with conventional supports.

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P.07 Design of multifunctional µ-carriers by electric field-assisted atomization

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IMCB and DSCTM, National Research Council of Italy, Italy

Introduction

Spherical-shaped particles have gained much interest due to their many existing and potential applications which often require microspheres with a narrow size distribution as well as strict control of particle shape. Comparing to current techniques, Electric Field-assisted Atomization Process (EFAP) is a not invasive technology able to produce mono dispersed microparticles with high morphology control and sample repeatability. In this process the drops formed, starting from the Taylor cone, are generated by a sharp break of the jet as a result of the electric field forces (Patent No. WO 2009/143947 A1). This work is aimed to verify the use of EFAP process to develop alginate microspheres, which can be potentially used as carrier for drug delivery.

Materials and Methods

Alginates from brown algae, with different viscosities (250 and 20000 – 40000 cps) were processed to obtain micrometric round-like balloons. Aqueous alginate solutions - from 0.5 to 2% wt/v - have been atomized by applying high voltage electric field on the polymer jet at the needle tip. Different voltage and feed rate have been applied to optimize the size and shape of balloons which have been then fixed by directly collecting into a calcium chloride solution acting as crosslinking bath. The effect of alginate viscosity, flow rate and needle size, on drop formation and consequently on the shape and size of microparticles, have been qualitatively investigated by optical microscopy observations and quantitatively by using image analysis software.

Results and Discussion

EFAP technique allows producing narrowly dispersed crosslinked balloons with sizes ranging from 385 µm to 1 mm. They switch from quasi-spherical shaped particles (for lower voltages and flow rates) to perfectly spherical particles (for higher voltages and flow rates). At lower alginate concentrations, the presence of "tails" or protrusions is detected, due to instability effects occurring before droplets are collected in the crosslinking bath. In the case of high concentrations, particles even show a spherical shape with regular boundaries, without any protrusion typically present at lower concentrations. Furthermore, we have also investigated the influence of needle diameter on the carrier morphology. By comparing µ-ballons obtained by using 18 G (outer diameter 1.2 mm) and 27 G (outer diameter 0.4 mm) needles, we recognize a drastic decay in the balloon size in the latter case, independently upon the other EFAP parameters. As pilot study, Gelatin has been also included in Alginate microparticles to design µ-shuttles able to influence the cell microenvironment via controlled gelatin delivery. We verify that composite µ-ballons evidently swell in water - ca. three-fold increases their starting volume - assuring a gradual release of protein by combined diffusion and swelling mechanisms. This confirms that EFAP is a low-cost and high-productive technology to fabricate polymeric and composite µ-carriers suitable to influence in vitro cell microenvironment.

P.08 Morphological investigation of PCL and gelatin fibres in simulated culture conditions

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Institute of Composite and Biomedical Materials and DSCTM/CNR, Italy

Introduction
Polymeric fibres are currently one of the most intensively studiedmaterials for applications in biomedical areasas carriers for cell cultivation, drug delivery systems, or for enzyme immobilization. Currently, electrospinning is the most interesting technique to produce them because it offers numerous opportunities to manipulate and control surface area, fibre diameter andfibre density.The aim of this study is to investigate the morphology of bi-component Polycaprolactone (PCL)/Gelatin electrospun fibres by the use of Scanning Electron (SEM) and Atomic Force Microscopy (AFM) to collect more information to better explain the mechanisms of cell/fibre interaction.

Materials and Methods
PCL and PCL/Gelatin fibres were successfully fabricated by using an automatic equipment (Nanon01, MECC, Japan) and then conditioned in simulated culture medium (SCM, i.e., Eagle's alpha minimum essential medium without protein serum) until 6 days. At the first stage, morphology of fibres was qualitatively investigated by Field Emission Scanning Electron Microscopy (FESEM) in low vacuum (LV) and environmental (ESEM) mode. Then, morphological and structural properties were quantitatively estimatedvia Atomic Force Microscopy (AFM) as a function of process conditions and post-treatments in order to evaluate the effect of Gelatin degradation on the fibre architecture at different times. Tapping Mode (TM) was employed to scan electrospun fibres surface whereas AFM imaging was performedat room temperature by using a silicon cantilever probe, a resonant frequency of approximately 320 kHz and a scan rate of 1 Hz. Mean fibre diameter was calculated averaging 20 measurementsat different incubation times.

Results and Discussion
TM measurements show a random network of beadless fibres of untreated PCL and PCL/Gelatin electrospun membranes. Just after 1 day in SCM, irregular topographical features can be detected onto the fibre surface due to the beginning of Gelatin loss along the fibre surface.As a consequence a larger reduction of PCL/Gelatin fibres diameter respect to PCL ones is detected, as the SCM treatment goes on. Moreover, the spatial distribution of protein onto the fibre surface has been also examined by AFM phase imaging. Indeed, the phase lag allows to detect differences in material properties at different locations on the sample surface.In this case, AFM phase image highlights relevant phase contrast between PCL and Gelatin domains, ascribable to different surface stiffness and elasticity, with drastic changes at different times in SCM solution. Hence, these data suggest that Gelatin probably plays a complex role on the interaction with cells by modifying bioactivity and stiffness of fibres during in vitro culture.

P.09 Nanofibrous nonwoven mats of poly(ethylene terephthalate)/poly(lactic acid) blends with covalently attached trypsin

D M P Rodrigues[1], A J Guiomar[1], J M S Rocha[1], S C S Pinto[2], J A Lopes da Silva[2] and M Helena Gil[1]

[1]University of Coimbra, Portugal, [2]University of Aveiro, Portugal

Nanofibrous nonwoven mats (NNMs) prepared by electrospinning have been widely used in applications such as filtration, optoelectronics, sensing, drug delivery and regenerative medicine, owing to their high surface-area-to-volume ratio, porosity and interconnectivity, which can be easily controlled by adjusting solution properties and process parameters. As poly(ethylene terephthalate) (PET) is a non-reactive, nonexpensive polymer with good electrospinning, structural and mechanical characteristics, it can be used in the preparation of membranes exhibiting concurrent biocatalysis and separation, for applications in the agro-food and pharmaceutical areas.

However, the absence of reactive groups and the hydrophobicity of PET preclude its use as a matrix for covalent enzyme immobilization. With the aim of introducing reactive groups and decreasing the hydrophobicity of PET, we blended PET with different types of branched
poly(lactic acid) (PLA). These blends were electrospun and trypsin, a proteolytic enzyme, was covalently attached to the resulting NNMs. The morphology of the mats and their chemical composition was evaluated by scanning electron microscopy and infrared spectroscopy, respectively, and their hydrophobicity was assessed by contact angle goniometry and water sorption capacity. Additionally, tensile testing, differential scanning calorimetry and thermogravimetric analysis were used to evaluate their mechanical and thermal properties. Trypsin could be covalently attached to the PET/PLA mats, exhibiting proteolytic activity.

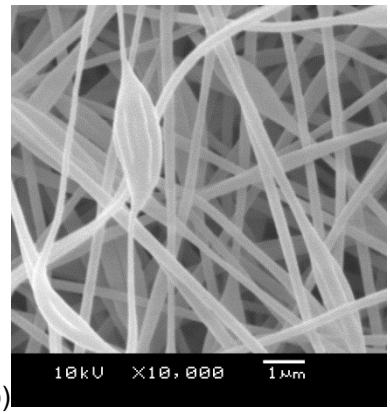
P.10 Core-shell carbon-ceramic fibres by electrospinning and atomic layer deposition (ALD) for fuel cell catalyst supports

P Heikkilä, A Pasanen, K Heikkinen, M Putkonen and M Vähä-Nissi.

VTT Technical Research Centre of Finland, Finland

Electrospinning can be used to prepare submicron polymeric or composite fibres. Such fibres can be as precursors and subsequently pyrolysed into carbon fibres. The small fibre diameter, small pore size, and high surface area of the nanofibre web are properties that are advantageous for various applications including catalysis. In this study we prepare corrosion resistant and electrically conductive catalyst support structures utilizing electrospinning.

In this presentation we present first results of the study carried out within project Catapult (novel CATAlyst structures employing Pt at Ultra Low and zero loadings for auTomotive MEAs; Supported by EU FCH-JU; Grant agreement no 325268). Our approach to produce core-shell carbon-ceramic catalyst supports include preparation of electrospun precursor fibres, stabilization and carbonization of precursor fibres into carbon, and atomic layer deposition (ALD) coating method to produce semi-conducting oxide layer onto carbon fibres. Electrospun fibre sheets are prepared from polyacrylonitrile (PAN) and mixture of PAN and carbon nanotubes (CNT) with lab scale electrospinning setup equipped with rotating drum collector in dry atmosphere (Fig 1). Stabilization and carbonization of web samples are carried out using tubular furnace suitable for roll-to-roll operation, and carbon samples are coated with niobium doped titanium oxide in ALD batch reactor (Fig 2).

a)  b) 

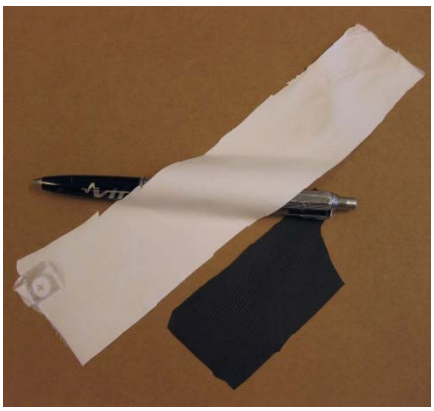
c) 

Figure 1. a) Electrospinning equipment, b) image of PAN fibres and c) electrospun and stabilized PAN web.

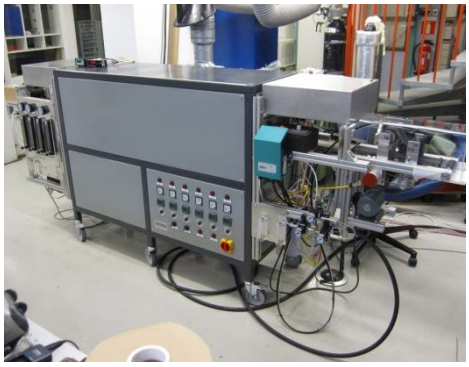
b)  c) 

Figure 2. Facilities for a) electrospinning, b) heat treatment and c) ALD.

P.11 Optical noninvasive method for rapid determination of alignment degree of oriented nanofibrous layers

J Klemes, M Pokorny, J Rebicek and V Velebny

Contipro Biotech s.r.o., Czech Republic

Nanofibrous materials with regular structures prepared by an electrostatic spinning method may be utilized in optical and electronic applications, tissue engineering and regenerative medicine. A rapid noninvasive method for an initial estimation of nanofiber orientation degree in materials during their mass production is needed.

Thin layers of such materials exhibit no significant light absorption features in the visible region, but polarized light of a specific wavelength is modulated by a basic optical light-matter interaction occurring when the light passes through the system. Two different alignment degree determination methods utilize these interactions with almost perfectly aligned, crossed and randomly oriented polymer nanofiber structures are presented in this work.

The first of them is based on the attenuation of linear polarized light by a nanofibrous oriented layers with definite thickness. The attenuation is highly dependent on the angle between linear light polarization direction and the main alignment nanofiber axis and alignment degree in the oriented structure. The other method uses Fourier optics principles and an analysis of CCD captured diffraction patterns. These dependences are compared with usual anisotropic structural properties obtained by scanning electron microscope image analysis.

We present a rapid and objective noninvasive method for the evaluation of anisotropic properties of nanofibrous materials during and after their production process. Instead of the commonly used electron microscopy image analysis this approach allows observing and estimating alignment degree in a macro scale and shorter time.

P.12 Electrospun PAN/PVDF composite for Li-ion battery separator

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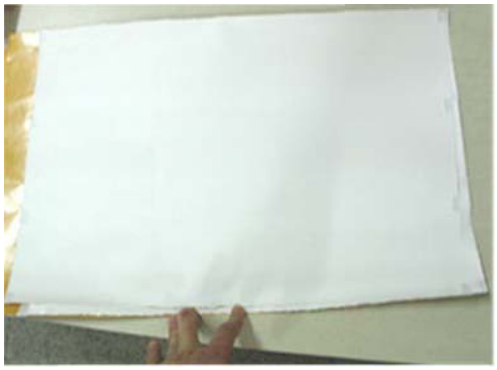
[1]Tianjin Polytechnic University, China, [2]Key Laboratory of Advanced Textile Composites of Ministry of Education, China, [3]University of Alberta, Canada

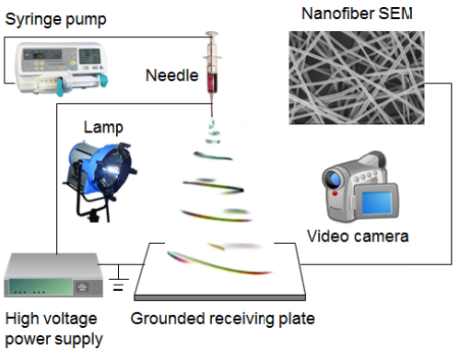
The electrospun nanofiber membrane has excellent perfomance when used as separator of Li-ion battery, its applications were limited, however, due to the low cohesive force between single nanofibers and the low strength of the electrospun membrane. In this study, the PAN-PVDF electrospun membrane was prepared via co-electrospinning with thermostable phase PAN and low melting temperature phase PVDF. The PVDF component partially melted to form point-bonds after proper thermal calendering process and relevant properties were measured. The results showed that the strength of the modified membrane was almost 10 times higher than that of as-spun electrospun membrane, slightly inferior to CELGARD 2400. The improvements in electrochemical

properties of the electrospun samples were also observed in this study such as, (1) ionic conductivity at room temperature was 1.32×10^{-3} S/cm; (2) electrochemical stability potential was 5.24 V; (3) interface impedance between the membrane and the electrodes was 45Ω; and (4) the initial discharge capacity was 152mAh/g under 0.2 C ratio. Therefore, the comprehensive properties of electrospun membrane were found to be superior to those of the modified CELGARD 2400.

Keywords: Co-electrospinning; PAN/PVDF; Point bonding; Li-ion battery separator



Principle of single needle electrospinning



Electrospun PAN/PVDF battery separator

P.13 Electrospinning polymers for tissue engineering applications

Z McCrea[1], Y Arnanthigo[1], S Cryan[2], M Maguire[3] and S O' Dea[1,3]

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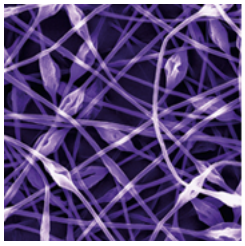
The fabrication of scaffolds for tissue engineering (TE) applications is a rapidly growing area. However, limitations of the methods used to date include difficulty producing large pore sizes (to enable cell penetration through the scaffold), and the identification of organic polymers that have mechanical properties similar to synthetic polymers. Electrospinning polymers is a widely used technique for the generation of nanofibrous scaffolds for TE. In addition, Mesenchymal Stem Cells (MSC) are an important cell source for TE. These cells have the potential to self renew and differentiate into numerous cell types including; osteoblasts, chondrocytes and adipocytes. The aim of this project is to use a novel jetting system, Spraybase® developed by Profector® Life Sciences, to generate innovative, safe, 3D scaffolds that have large pore sizes and also have biochemical characteristics suitable for supporting and enhancing MSC growth and survival in a cell culture environment.

Poly(ethylene oxide) PEO is an FDA-approved polymer that has been shown to be capable of producing scaffolds with large pore sizes. However, PEO is water-soluble, resulting in a limited life span in cell culture medium. In order to delay the dissolution of PEO scaffolds, we combined PEO with MSC culture medium and a polysaccharide polymer, agarose which is generally extracted from seaweed. The agarose provides strength to the scaffold while also making it durable to last in a moisture environment. Addition of MSC culture medium to the scaffold adds the nutrients required for MSC to remain viable once seeded onto the scaffold.

We have electrospun novel 3D PEO/agarose/MSC culture medium scaffolds using the Spraybase® system, thus successfully integrating PEO into scaffolds suitable for supporting MSC growth and survival. Future work involves the addition of bone marrow-derived mesenchymal stem cells (BMSC) to the scaffold. The ability of these cells to infiltrate and disperse into these 3D matrices will be evaluated and their ability to continually differentiate into multiple cell types will be determined.



Electrospinning, Principles, Possibilities and Practice 2013

P.14 A new experimental approach to the study of multiscale structural development in polymers

G R Mitchell, D L Garcia, F J Davis and D Bowron

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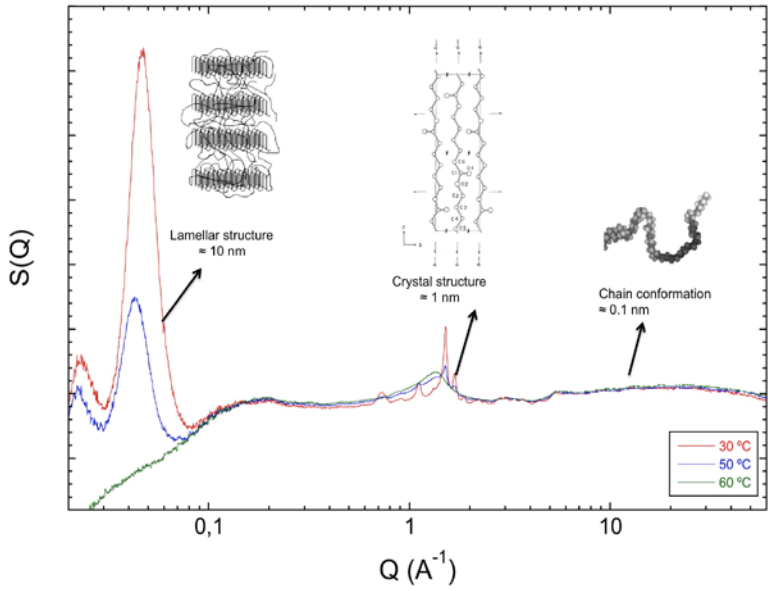
We use new neutron scattering instrumentation to follow in a single quantitative time-resolving experiment, the three key scales of structural development which accompany the crystallisation of synthetic polymers. These length scales span 3 orders of magnitude. The Figure shows the clarity and the extent of the data.

Figure: Time-resolving neutron scattering data for poly(ε-caprolactone) during cooling from the melt revealing the variation in the structure related to the three key length scales for crystallisation.



The study of polymer crystallisation dates back to the pioneering experiments of Keller and others who discovered the chain-folded nature of the thin lamellae crystals which are normally found in synthetic polymers. The inherent connectivity of polymers makes their crystallisation a multiscale transformation. Much understanding has developed over the intervening fifty years but the process has remained something of a mystery. There are three key length scales. The chain folded lamellar thickness is ~10nm, the crystal unit cell is ~1nm and the detail of the chain conformation is ~0.1nm. In previous work these length scales have been addressed using different instrumention or where coupled using compromised geometries. Most recently time-resolved x-ray experiments have revealed the possibility of new phenomena in the very early stages of crystallisation. Although there is now considerable doubt on such experiments, it draws attention to the basic question as to the process of crystallisation in long chain molecules. We have used NIMROD on the second target station at ISIS to follow all three length scales in a time-resolving manner for poly(ε-caprolactone). We show the capabilities of this new instrument and present the preliminary results on the development of a multiscale model of the crystallisation process in polymers.

P.15 Electrospun polyethylene oxide fibres containing carbon nanotubes

M Nazhipkyzy[1], S D Mohan[1], F J Davis[1] and G R Mitchell[2]

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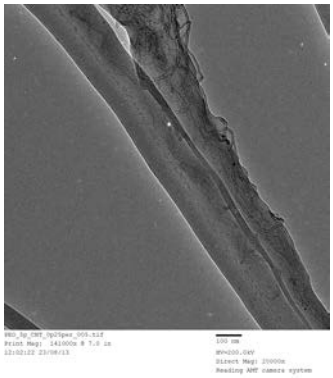
Carbon nanotubes have gained much attention in the last two decades with numerous publications reporting on their abundant properties ranging from thermal, optical, electrical and mechanical [1]. Carbon nanotubes are essentially a sheet of graphene wrapped into a cylindrical tube shape which can either have a single or multiple walls to give SWNT and MWNTs respectively. The tubes diameters are typically of the order of several nanometres, but they can be micrometres in length. Due to their unique properties they offer promise in a multitude of potential applications, especially in composite materials with a large portion of current research on these materials dedicated to embedding them in a polymer matrix. It is found that electrical and mechanical properties are improved parallel to the tube axis rather than perpendicular; thus it is crucial for the nanotubes to be aligned within the matrix if improvements to the properties are to be obtained [2]. This constraint presents a major challenge as strong intermolecular forces causes nanotube agglomeration; furthermore their insolubility in most common solvents leads to poor dispersion and random orientation within a typical polymer matrix.

In these investigations we have taken carbon nanotubes and attempted to align them within fibres produced through electrospinning. Electrospun fibres offer some useful applications such as in electronics, biomedical applications, textiles and composite materials [3]. The use of carbon nanotubes embedded in the fibre can be used to improve the fibres properties making it more attractive for use.

Using multi-walled carbon nanotubes (MWCNTs) we have attempted to confine and align the carbon nanotubes within polyethylene oxide (PEO) nanofibres. We have used a variety of PEO molecular weights, MWCNT/PEO concentrations and observed the effect on the fibre morphology using SEM and the confinement and alignment of the nanotubes in the TEM. Solutions were prepared in water and in some cases a surfactant, Triton X-100 was added to aid in the dispersion of nanotubes throughout the solution. The relationship between preparation conditions and nanotube alignment is described.



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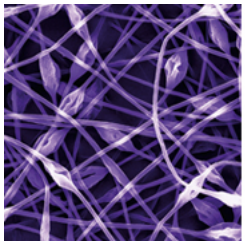


P.16 Fibrous scaffolds for neural tissue engineering in the auditory system

K Ngamkham[1], P Viswanathan[2], E Themistou[3], M Rivolta[4] and G Battaglia[1]

[1]University College London, UK [2]King's College London, UK, [3]Queen's University, Ireland, [4]University of Sheffield, UK

Hearing loss is one of a high prevalent impairment worldwide. It affects people in a broad age range since the causes and risk factors are varied. At present, some types of hearing impairments have a palliative treatment whereas some, especially for those where otic neurons are damaged, cannot be properly treated. Recent findings had shown it possible to use human embryonic stem cell-derived otic neural progenitors (ONPs) as a new mode of treating hearing loss caused by damage to the spiral ganglion neurons (SGNs). To improve the efficiency and overcome some limitations of this treatment, the concept of tissue engineering, which involves an interaction between cells and scaffold, the matrix-mimicking construct, should be applied. Here, we describe the influence of poly(l-lactic acid)(PLLA) aligned fibers on ONP cell morphology, proliferation, neuronal differentiation and establishment of neural polarity in both progenitor and neuralising conditions. The results show that most of ONPs on aligned fibers exhibited bipolar morphology and extended their neurites along the major fiber axis. Their proliferation was lower than those in 2D culture but the differentiation of ONPs on aligned fibers was enhanced in both progenitor and neuralising conditions as indicated by the fluorescence intensity and number of cells that were positive for neuronal markers (β-tubulin III and NF200). Moreover, axonal and dendritic markers (TAU and MAP2 respectively) were also induced after 14 days in culture.

Furthermore, the PLLA fibers can be surface functionalized using amphiphilic block copolymers of poly(lactic acid)(PLA) -poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC) and poly(lactic acid)(PLA) – poly[oligo (ethylene glycol) methyl ether methacrylate] (POEGMA) to generate cell inert hydrophilic fibers. By conjugating cell adhesive peptides such as RGD to the hydrophilic block (e.g. POEGMA), could be enhancing both cell adhesion and alignment.

P.17 Regulation and safety mechanisms of the 4SPIN® technology

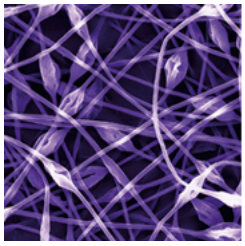
M Pokorny, J Novak, J Rebicek and V Velebny

Contipro Biotech s.r.o., Czech Republic

There are many parameters affecting the formation of nanofibrous layers in electrospinning method such as the solution properties, the process parameters, the geometry of electrodes and the ambient conditions. The production of nanomaterials of repeatedly the same properties (for example fiber diameters, layer thicknesses etc.) is conditional upon the preservation of all production conditions in a controlled way and in the narrowest range. The solution properties and the geometry of the electrode arrangement are precisely adjustable but the process parameters and the ambient conditions need to be regulated by a suitable electronic system.

This work presents regulated process parameters and their tolerances, i.e. it describes a regulation of the high voltage, the feeding rate, the temperature and the velocity of the air flow, the collector speed, the time of deposition etc. The regulated parameters inside of the 4SPIN® laboratory device are accompanied by the record of the measured parameters like the current of the high voltage branch, temperature and humidity in the deposition chamber. The 4SPIN® central control system performs automatic functions associated with the safety features such as automatic mechanism for the residual surface charge discharging, safety lock of the chamber sliding door etc.

It is possible to create reproducible nanomaterials of the same properties due to the implementation of the precisely regulated process parameters. The 4SPIN® central system simplifies the control and also improves the productivity and the operator safety.



P.18 Introduction of new laboratory device 4SPIN® for nanotechnologies

M Pokorny, J Rebicek, J Novak, J Klemes, J Rusickova and V Velebny

Contipro Biotech s.r.o., Czech Republic

New desktop laboratory apparatus 4SPIN® have been developed for deposition of nanomaterials dedicated to medical applications. The apparatus integrates different methods to enable preparation of nanostructured scaffolds according to researching demands. These methods are Electrospinning, Electrospraying, Electroblowing and Solution spinning.

Almost twenty different materials (including hyaluronic acid and its derivates) have been processes so far. Precisely aligned nanofibers with anisotropic properties have been collected by advanced Electrospinning. Small balls structures have been prepared in the Electrospraying mode. Morphological properties could be well controlled by Electroblowing process parameters, for example reduction of fiber diameter down to 50 % is obtained.

The device is designed to be run in a clean room (variety of accessories are able to be sterilized). Stable accurate processes lead to preparation of material with high repeatable and reproducible properties. Thanks to safety components, easy handling, intuitive device control and other benefits the apparatus significantly contribute to accelerate research progress in the medical application field.

P.19 Production of $GdBa_2Cu_3O_7$-x Nanofibers by electrospinning method

S Ezadpanah, A Qalambor Dezful and M Zargar Shushtari

Shahid Chamran University, Iran

In this thesis $GdBa_2Cu_3O_7$-x(a high temperature ceramic superconductor) nanofibers from a precursor polymer solution are produced, using electrospinning method. Precursor polymer water solution containspolyvinylpyrrolidone (PVP) and a mixture of *Gadolinium* nitrite, Barium nitrite, and cupper nitrite with mass ratio of 5/1 (polymer/nitrite). Using above method (electrospinning) and with following condition; solution density of 55%, voltage of 18 kV, distance between collector plate and nuzzle of 12 cm and injection solution rate of 1 ml/h, fibers with diameters of the order of 470 nm and average length of greater than 10 µm are produced. The SEM pictures of $GdBa_2Cu_3O_7$-x fibers indicate that with increasing the potentials, the distance between collector plate and nuzzle, and solution density the diameter of fibers will reduce, however with increasing the injection solution rate the diameter of fibers will increase. For nitrogen liberation, the produced fibers are heated to a temperature of 200 oc and kept at this temperature for 12 hours. The SEM pictures at this stage indicate that the fiber diameters are increase to about 1 µm. This diameter increased of the fibers could be predicted with understanding of the reaction between citric acid and nitrites.

After this step the calcination processes are done on the fibers at a temperature of 900 centigrade degree. Following the calcination, in order to achieve a superconducting phase transition, the fibers were subjected to a cooking process in a temperature of 930 centigrade degree for 12 hours. X-Ray diffraction patterns of the cooked sintered samples indicate that the $GdBa_2Cu_3O_7$-x superconducting phase are created. The SEM pictures, at this stage, indicate that after sintering process the acquired fiber diameters are largely decreased. Finally with the use of measurement software, the average diameter of produced nanofibers is estimated to be of the order of 90 nm.

P.20 Study on stabilization of electrospun polyacrylonitrile nanofibers as carbon nanofibers precursor in different temperatures

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Shahid Chamran University, Iran

In this work electrospun polyacrylonitrile (PAN) nanofibers was obtained from PAN and N,N-dimethylformamide (DMF) solution. Electrospining conditions were as followed: polymer solution consentration was 14% wt, needle to collector distance was 15 cm, voltage and flow rate were 10kV and 0.2 ml/h respectively.

PAN nanofibers after heat treatment, that led to both stabilization and carbonization, will be turned to carbon nanofibers. Because of importance of carbon nanofibers many works have been done to optimize heat treatment processes of PAN nanofibers. Stabilization is the most important step and the heart of the carbon nanofiber production. To achieve the more stable PAN nanofibers and consequently carbon nanofibers with the best mechanical properties, stabilization has been performed in different temperatures, and then effect of temperature on cyclization degree of nanofibers has been studied.

Electrospun PAN nanofibers have been stabilized at 200,220,240,260 and 280 C in a cylindrical furnace that its temperature was increased with a rate of 1 C/min in Oxygen atmosphere for 1 hour. From scanning electron microscope (SEM) images it was observed that PAN nanofibers diameter were about 500 nm. From differential scanning calorimetry (DSC), it was concluded that nanofibers that were stabilized in higher temperatures had more cyclization degree, such that after heat treatment at C for 1 hour this parameter increased to 84.6%. Moreover, fourier transform infrared (FTIR) spectroscopy results showed that due to heat treatment a peak in 805.86 cm^{-1}has been appeared that was contributed to C C band of carbon structures.

Keywords: “electrospinning; Polyacrylonitrile; carbon nanofiber; stabilization; cyclization degree”

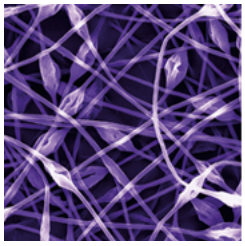
P.21 Study on the effect of diameter size of electrospun ZnO nanofibers as a photo anode on the efficiency of CdS Quantum dot sensitized solar cells (QDSSCs)

A Qalambor Dezful, F Ghazizadeh and A Ghalambordezfuli

Shahid Chamran University of Ahvaz, Iran

In this research a progress report of ZnO nanofibers production process with the goal of application in QDSSCs by electrospinning method is presented. In the recent years, ZnO as a wide band gap semiconductor has attracted for many applications, specially suitable for n-type electrode materials of solar cells. When a 1-D ZnO (like nanofibers) is used as a n-type electrode, it has a number of advantages, such as a high transmittance in the visible wavelength region, a larger surface area and the high electron mobility along the growth direction, and in result these structures enhance the efficiency of the solar cells. In this paper, at the same time producing the electrospun ZnO nanofibers, the voltage applied to the needle (15, 16, 17, 18 kV) and the distance of the needle to the collector (5, 10, 15, 20 cm) were investigated as an independent variables and the diameter of ZnO nanofibers was as a dependent variable. Also to finding a relationship between these parameters, the factorial design and regression method of SPSS 16 software has been used.

In conclusion all the result show, we can control the size of fibers diameter and able to produce nanofibers in the range of a few hundred of nanometers. These nanofibers (on the FTO substrate), after the heat treatment at 500oC and sensitizing to CdS quantum dots by 5 circle SILAR method, will be turned to photo anodes. Every anode with a cathode and the polysulfide electrolyte, were attached together and make a solar cell. The results of I-V diagrams of all the solar cells has been demonstrated, the cell with the minimum of nanofibers diameter, has the maximum of efficiency and the short circuit current. Finally, all the nanofibers and quantum dots in this paper were investigated by SEM and TEM methods respectively to study their morphology.



P.22 Production of composite nanomaterials using 4SPIN® technology

J Rebicek, M Pokorny, A Kotzianova and V Velebny

Contipro Biotech s.r.o., Czech Republic

Electrospinning is a relatively simply, universal and an effective fabrication technique to produce nanofibers diameters ranging from 50 nm to several micrometres from polymer solutions or melts. In a typical electrospinning set up, only electrospun nanofibers from one material are produced. However, a further improvement of the electrospinning arrangement allows producing nanofibrous layers composed of different types of polymers and so leads to enhance materials properties.

New desktop laboratory apparatus have been developed for nanofiber production from solutions of synthetic and natural polymers. The apparatus integrates different methods to enable preparation of nanomaterials according to researching demands. These methods are Electrospinning, Electrospraying and Electroblowing.

4SPIN® has five types of emitters for composites materials, which can be used to electrospinning of two or three different types of polymers simultaneously onto the same collector. The simplest method is to use a needle jet emitter. It forms high gradient of the electrostatic field surrounding the drop of the polymer solution and so leading to the highest spinnability. Another approach is needleless electrospinng principle capable of scale-up of the nanofibrous materials production. To obtain a homogeneity mixed nanofiber layers, the nanofibers can be directly collected on the rotating drum. Another advanced type of 4SPIN® emitters is a coaxial single needle jet. By using the co-axial electrospinning method , it is possible to produce hollow fibers and even core materials that will not form fibers via electrospinning.

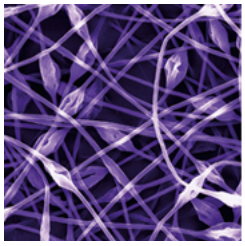
Thanks to implemented methods and different types of emitters the apparatus can produce the composite a hybrid nanostructures to improve the final quality of the material and significantly contribute to accelerate research progress in the material application field.

P.23 Electrospinning of hyaluronic acid by 4Spin® technology

J Ruzickova, K Knotkova, M Pokorny, J Novak and V Velebny

Contipro Biotech s.r.o., Czech Republic

The use of hyaluronic acid (HA) in medical devices is very tempting because it is a natural biodegradable polymer improving migration and proliferation of the cells and a production of the extracellular matrix. The nanofibrous form of the mass brings benefits such as a high reactivity given by the large specific surface, a high efficiency in protection against bacteria and viruses given by the small pore size and a possibility to easy incorporate an additives like drugs encouraging to develop medical devices based on hyaluronic acid or its derivatives. The processing of hyaluronic acid into the nanofibers is quite difficult because HA water solutions reach the high viscosity even at a low polymer concentration and form a gel. The solutions of even lower concentrations are not spinnable due to insufficient entanglement of the polymer chains. The 4Spin® technology allows to spin a hyaluronic acid of both, a low molecular weight and a high molecular weight, into different structures enabling to produce a wide scale of nanofibrous materials of various properties covering the specific needs of the different applications in field of wound healing, tissue engineering and drug delivery. The mentioned production method is a highly productive and stable. The use of hyaluronic acid derivatives results in a nanofibrous materials with a great sorption ability suitable for the treatment of chronic wounds. Such medical device assures a moist wound healing with all its benefits and it may also release antimicrobial substances eliminating the wound contamination.



P.24 Effect of NaY zeolite content on electrospun PVDF/NaY fiber meshes membranes for biomedical applications

A C Lopes[1], C Ribeiro[1], V Sencadas[1,2], G Botelho[3] and S Lanceros-Méndez[1]

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Electroctive polymer composites are a subject of large scientific and technological interest. In particular, zeolites as filler allow tuning composites electrical response, chemical stability, catalytic and antibacterial activity. Further, preparing the composites by electrospinning allow larger interaction surface areas, increasing materials efficiency for applications in tissue engineering, filtrations membranes and sensors, among others. Poly(vinylidene fluoride) (PVDF) electrospun membranes have been prepared with different NaY zeolite contents up to 32%wt. Inclusion of zeolites induces an increase of average fiber size from ~200 nm in the pure polymer up to ~700 nm in the composite with 16% zeolite content. For higher filler contents, a wider distribution of fibers occurs with an almost bimodal size distribution between the previous size values. Hydrophobicity of the membranes increases from ~115º water contact angle to ~128º with the addition of the filler and is independent on filler content. The water contact angle further increases with fiber alignment up to ~138º. Electrospun membranes are formed with ~80% of the polymer crystalline phase in the electroactive □ phase independently on the electrospinning processing conditions or filler content. Viability of MC3T3-E1 cells on the PVDF membranes after 72 h days of cell culture indicate the suitability of the membranes for tissue engineering applications.

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P.25 Electrospun silk-elastin-like fiber mats with potential application for tissue engineering

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Protein-based polymers are present in a wide variety of organisms fulfilling structural and mechanical roles. Advances in protein engineering and recombinant DNA technology allow the design and production of recombinant protein-based polymers with an absolute control of its composition. Silk-elastin-like polymers (SELPs) are a new class of bioinspired, biologically synthesized copolymers, composed of alternating silk and elastin blocks. In the present work, we report the electrospinning of SELP-59-A with formulation (S5E9)9, where S is the number of silk blocks (GAGAGS) and E is the number of elastin blocks (VPAVG). Electrospinning was performed using formic acid solutions at different SELP-59-A concentrations without adding further agents. The size and morphology of the electrospun structures was characterized by SEM showing to be dependent of concentration and solvent used. While low concentrations lead to the formation of microsized spherical structures, higher polymer concentrations produced electrospun fibers with increasing diameter and size distribution, ranging from the nano to the sub-microscale. Treating the electrospun mats with methanol showed to promote water insolubility through a conversion of random coils into beta-sheets (FTIR). The methanol-treated electrospun membranes were characterized in terms of its wettability, displaying a water contact angle of 69 º, a degree of swelling in the range of 570-720% and water vapor transmission rate of 1083 g/m^2/day. The mechanical properties measured by uniaxial stress-strain analysis revealed an average modulus of elasticity of ~126 MPa. Furthermore, the produced electrospun SELP-59-A fiber matrices demonstrated to be non cytotoxic and able to support adhesion and proliferation of normal human skin fibroblasts. These properties indicate that SELP-59-A membranes have potential to be applied as wound dressings for skin regeneration purposes.

P.26 Structural and morphological control of electrospun polymer and carbon nanofibers

C S Sharma

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Electrospinning has been widely used to fabricate the polymer nanofibers due to its added advantages over the other processes such as drawing, template synthesis and self-assembly. By tuning the various process and solvent parameters, one can easily control the structure and morphology of electrospun nanofibers. We will present an overview of various methodologies used in our research group to control the morphology of electrospun nanofibers with an emphasis on carbon nanofibers. Some of the polymers which are precursors of carbon and thereby of our interest include Polyacrylonitrile (PAN), Polymethamethylacryalte (PMMA), Polystyrene (PS) and an epoxy based negative photoresist (SU-8).

1. A combination of non-solvent induced phase separation (NIPS) phenomenon with electrospinning is proposed to fabricate highly porous polymeric nanofibers. As compared to conventional electrospinning, polymeric nanofibers fabricated by this method have almost an order of magnitude increased specific surface area owing to the porosity generated on the surface as well as interior of these nanofibers.

2. The modified electrospinning (in combination with NIPS) technique is extended to core shell electrospinning in order to fabricate hollow fibers having a highly porous sheath di ectly in one step.

3. Porous and rough PS fibers were fabricated by using the mixed solvents. With the different vapor pressure of two solvents used, vapor induced phase separation took place during electrospinning that leads to the formation of rough morphology with internal porosity.

Further we will discuss the surface modification of these rough and porous nanofibers using chemical route for different applications. Some of the applications being pursued in our group will be discussed such as:

1. Use of rough and porous polymer nanofibers as carrier for biomedical applications
2. Surface Patterning to fabricate micro-array of carbon nanofibers to be used as electrode materials
3. Using the multiscale polymeric nanofabric for environmental remedial application.

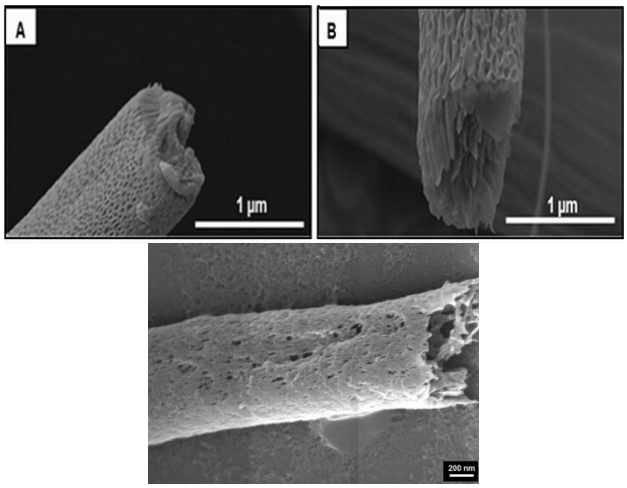
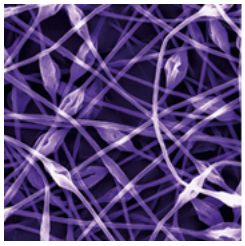


Figure: SEM images of rough, porous and hollow electrospun polymer and carbon nanofibers



P.27 In-situ measurement of adhesion between electrospun fibers

U Stachewicz, F Hang, and A H Barber

Queen Mary, University of London, UK

Adhesion at small length scales is of fundamental importance in the functionality and design of nanomaterials. Nonwoven materials containing fibres produced by electrospinning are used extensively as 2D in-plane networks in filtering membranes and medical applications such as tissue scaffolds, where adhesion between fibres influence their mechanical properties and flexibility.

This work utilizes novel experimental techniques to apply forces to separate individual electrospun fibres contacting one another using atomic force microscope (AFM) in combination with scanning electron microscope (SEM). Such an experimental setup is powerful in examining adhesion mechanisms directly for individual fibre diameters below 1 micron. These experiments provide a quantitative insight into the adhesion between electrospun fibres in a network that is representative of membrane in-plane loading conditions found in electrospun membranes used for filtration and tissue engineering applications.

P.28 Composite electrospun nanofibres for treatments of air and water

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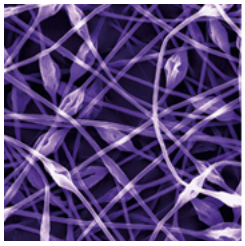
The objective of the work is to develop composite nanofibres suitable for filtration of air and water by merging biopolymer processing and sol-gel techniques using electrospinning technology. In particular the attention will be focused on the production of innovative multifunctional filter media by integrating keratin nanofibre membranes with inorganic nanoparticles (as nanometals or nanometal oxides). Among the functional polymers, bio-based polymers as proteins (keratin or fibroin) or carbohydrates (chitosan), offer an attractive solution for the preparation of nanofibrous membranes able to adsorb heavy-metal ions, dyes and VOCs.

The advantage of keratin-based nanofibre membranes is that they can offer both removal of suspended small particles filtration (due to the controlled porosity and small pore size) and adsorption of heavy-metals, dyes and VOCs, such as formaldehyde (due to the presence of many functional groups able to bind toxic substances). Nanometals and/or nanometal oxides improve membrane functionalities towards removal of bacteria (antimicrobial, low bio-fouling) and exploitation of photocatalytic reactivity (removal of drugs, antibiotics, pesticides, and fertilizers), respectively.

The keratin nanofibrous membranes (Figure 1) were tested as adsorbent of heavy metal ions. The pure keratin nanofibres showed excellent adsorption performances for copper ions reaching removal efficiency of 90% and their selectivity for different metal ions follows the order Cu(II)>Ni(II)>Co(II). Keratin nanofibre membranes were also tested as adsorbent of dyes. Methylene Blue was used as an organic dye. Keratin nanofibres showed a maximum adsorption capacity of 170 mg/g, reached at the initial MB concentration of 250 mg L^{-1}, pH 6, adsorbent dosage of 1g L^{-1} and contact time of 24 hours. Keratin nanofibres showed an adsorption capacity towards Methylene Blue of two order of magnitude higher than that of wool fibres, due to their high specific surface. Finally, the ability to remove airborne formaldehyde of keratin nanofibres deposited on the polypropylene conventional air filters was studied in order to test these membranes for active air cleaning. The keratin nanofibres are able to reduce the airborne formaldehyde concentration up to 100%.



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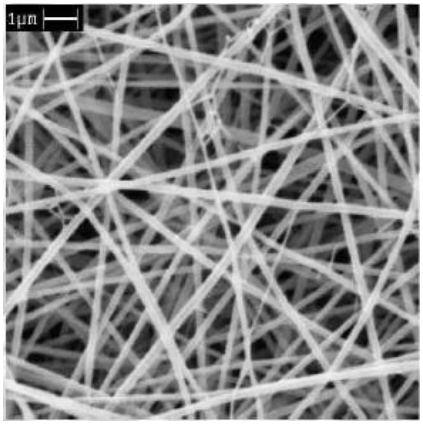

Figure 1. Electrospun keratin nanofibres.

In this work, different strategies will be followed to prepare nanoreactive membranes active for selective removal of different classes of pollutants in water and air treatment. In particular, electrospinnable keratin solutions doped with inorganic nanoparticles were prepared by mixing keratin solutions with Ag and TiO_2 nanopowder or Ag and TiO_2 nanosol (Figure 2).

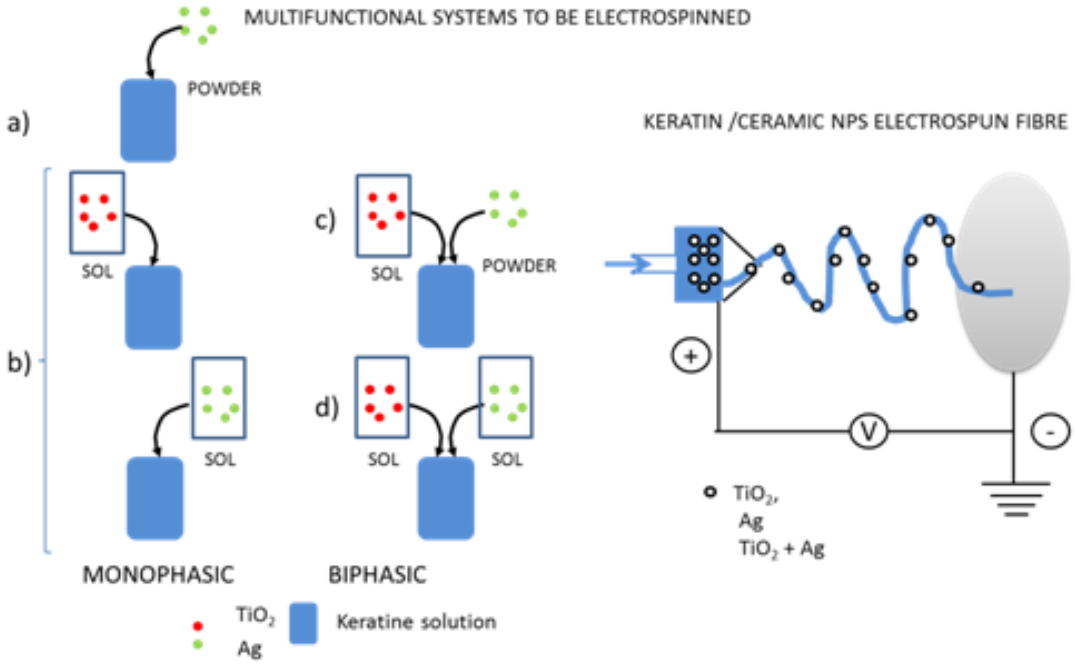

Figure 2. Scheme of the electrospinnable formulations.

The inclusion of inorganic nanoparticles, with antibacterial or with photo-catalytic/self-cleaning properties, in electrospun nanofibrous materials can transfer such new functions to final polymeric product towards the creation of hybrid multifunctional materials.

P.29 Growth of nanosized-copper benzene-1,3,5-tricarboxylate on electrospun crosslinked polyvinyl alcohol polyacrylic acid membrane

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Polyvinyl alcohol (PVA) is a water soluble polymer that has been extensively studied for electrospinning. PVA electrospun fibrous membranes with well-controlled uniform nano-sized fibre diameter have been tested for a range of applications. However, its disadvantage is that it is soluble in water and requires some form of cross-linking chemistry to make it stable in water. Electrospun PVA has been cross-linked by various methods including additives and post treatment chemistries to attain stability in water. Of interest is a study by Xiao et al (2010)[1], where they combined PVA with polyacrylic acid (PAA) to produce electrospun fibres which can be thermally stabilized by heating at 145°C for 30 minutes and also demonstrated that the membrane can extract copper(II) from an aqueous solution. The affinity of this membrane for copper (II) in liquid media makes it an ideal candidate for our purpose since the first step in the layer-by-layer growth of copper benzene-1,3,5 tricarboxylate (CuBTC) involves forming a layer of adsorbed copper.

Currently MOFs are incorporated into nanofibres by mixing the pre-made nano-MOF particles into the polymer solution prior to making the nanofibres (Ostermann et al 2011)[2]. As a consequence, this may cause a significant amount of MOF particles to be buried underneath the polymer fibre surface which may prevent the incorporated MOFs from participating in adsorption (e.g. toxic industrial agents) and therefore reducing the efficacy of the MOFs. In this study, we investigate the feasibility of growing MOFs onto the PVA/PAA electrospun fibre surface. After thermal treatment to stabilize the PVA/PAA membrane, a model MOF in this case, CuBTC is grown onto the fibre surface using a layer-by-layer deposition approach as described by Maksoud et al (2013)[3].

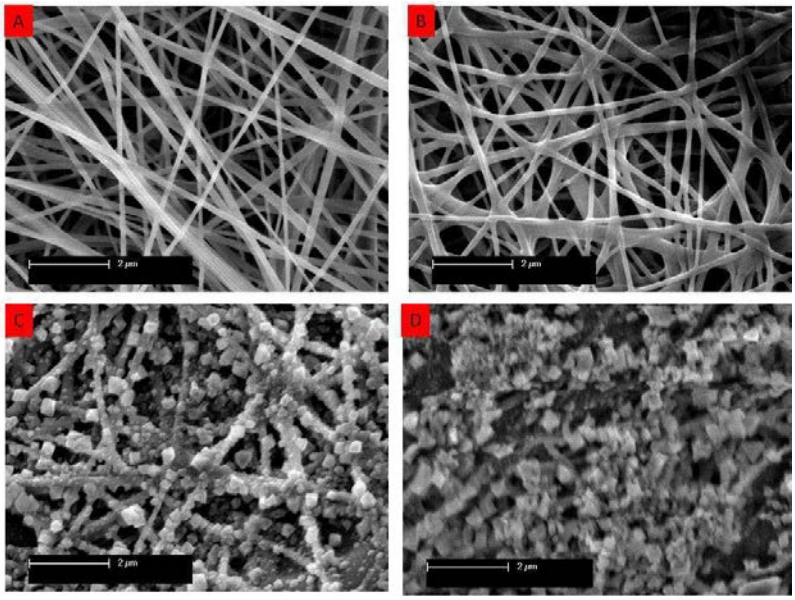

Figure 1. Electrospun PVA/PAA (A), electrospun crosslinked PVA/PAA (B), electrospun crosslinked PVA/PAA with CuBTC using diluted copper (C) and using saturated copper acetate(D)

[1] S. Xiao, M. Shen, H. Ma, R. Guo, M. Zhu, S. Wang and X. Shi, J. Appl. Polym. Sci., 2010, 116: 2409–2417.

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P.30 Atomic force microscopy and nanoindentation techniques for fast and effective control over the structure and mechanical properties of electrospun nanofiber meshes

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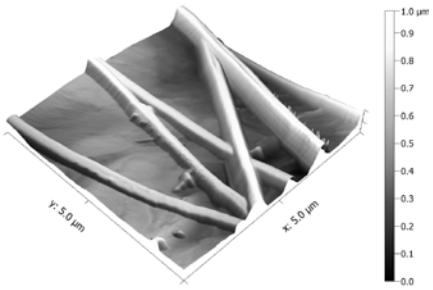
The Electrospinning method for production of nanofibers has become one of the most promising techniques for producing nanostructured materials with very wide range of applications. In order to ensure that the resulting electrospun products correspond to given requirements, standards and regulations we need to further expand and develop the quality control procedures. The present work represents a fast and effective method to control the nanostructure and mechanical properties of electrospun nanofiber meshes via Atomic Force Microscopy (AFM) and Nanoindentation investigation techniques.

The demonstrated AFM investigation methodology gives comprehensive information about the surface topology of the tested electrospun meshes. It provides data about the surface roughness, distribution, orientation, alignment and dimensions of the produced nanofibers. The AFM can also be used to examine the overall quality of the electrospun nanofibers and to give feedback on the production conditions.

Nanoindentation technique is being used to observe the changes in the mechanical properties (hardness and elastic modulus) of the investigated samples with variation of the production conditions, materials and fillers used for Electrospinning.

Keywords: Electrospinning, nanofibers, atomic force microscopy, nanoindentation, quality control.



P.31 Methods for measuring electrospun fibre diameters

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The diameter of an electrospun fibre is one of the most common morphological descriptions reported in literature alongside bead formation and the appearance of wet fibres. Some early work has been done on the creation of automated image analysis algorithms [1] and on the use of laser diffraction to measure fibre diameter [2]. Using a pre-release copy of a commercially available fibre analysis package[1] (Electrospinz Ltd.) this work examines the correct method for gaining a statistically accurate measure of the fibre diameter distribution for a sample of electrospun fibre. Recommendations will be given for the scale of each image, the number of measurements per image and the number of images chosen at random from the sample to provide an accurate representation.

Before comparison between a human operator and an algorithm, the algorithm must be suitably characterized. All measurements of fibre diameter from digital images will have a fundamental limit of precision that is related to the

physical size that a pixel represents. By defining an acceptable lower limit of accuracy the scale of the image is also defined. If an error of ± 5% is chosen for example then the smallest fibre on any image must be at least 40 pixels wide. This assumes that the measurement technique is accurate to a single pixel at each edge of the fibre. For the automated image analysis algorithm this assumption can be tested by generating idealized simulated images of electrospun fibre [1] and comparing the generation conditions to the image analysis algorithm results. The algorithm was able to consistently report an average diameter within 2 pixels of the true diameter, performing within the limits of precision for idealized images. This performance was further tested in a real world application by using electron microscope images of an SEM calibration grid of known dimensions.

The initial problem faced with manual measurement method is the ability of a human operator to identify the edge of a fibre using standard input methods. Visual identification is trivial for most humans but the use of a mouse pointer to identify the pixel that represents this image is not. A test image was created with varying scale bar sizes that were measured by a human and the automated software. The software always reported the exact scale bar length while the human averaged an error of 1 pixel.

Two samples of electrospun fibre were produced under different processing conditions. Electron microscope images were then taken by a technician following a prescribed method. The fibre diameter distribution was then manually measured by a number of human operators using a standard method and the time taken was recorded. The same images were processed using the image analysis algorithm for comparison. It was found that the average human operator could measure the sample image set in approximately 2.5 hours while the fibre analysis package could achieve the same results in less than 5 minutes including user interaction time. The fibre analysis software reported an average diameter of 303 nm compared to the average of the human operators at 281 nm where a single pixel is 7.25 nm in diameter. Therefore the software was within 3 pixels of the human values. The average diameter for each image varied by 32 nm for the software while human operators varied by 82 nm. The human variation within a single image was 35 nm, larger
than the difference between the software average and the human average. The software made 9926 diameter measurements over 10 images. The human operators averaged 171 measurements over 10 images.

The final stage of this work is concerned with the production of a protocol for obtaining accurate fibre diameter distributions either manually or using an automated procedure.

[1] M. Ziabari et al 2007 Nanoscale Research Letters, 2, 597
[2] C-T. Li and J. Tietz 1990 Journal of Materials Science, 25(11), 4694

[1] Electrospinz SEM Analyser software package by Electrospinz Ltd. (www.electrospinz.co.nz): release date 2014

P.32 Addressing issues of electrospinning nanofibres on textiles: Productivity, perturbation and adhesion

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Academic and industrial interest for electrospinning raised in the 1990s. Textile is considered one of the most important field for the application of electrospun nanofibres, but at least three issues have to be solved in order to fulfil industrial requirements: up-scaling of electrospinning, process stability and nanofibres adhesion to textiles.

Large-scale electrospinning systems should be designed to increase productivity, allowing continuous nanofibre production and deposition. One approach is the use of multi-nozzle electrospinning plant. In this work, several multi-nozzle electrospinning configurations (from 6 to 9 nozzles) were tested in order to study jet-jet interactions (electrostatic repulsion, alteration of whipping motion). A final electrospinning pilot plant equipped with 62 nozzles was designed and developed. Electrospun nanofibres were continuously deposited on a textile substrates, moved during electrospinning by a roll-to-roll system. The shifting speed of the substrate influenced thickness, porosity and density of the deposited nanofibre layers.

For filtration, clothing and protective textiles, electrospun nanofibres need to be deposited on a supporting substrate (usually textile materials such as woven fabrics or non-wovens) because of their limited mechanical properties. Textile materials are electrical insulator by nature. In this work, different process perturbations (i.e. stability of the jets, increase of Coulomb repulsive force between the jets, distribution of the deposition zones on the collector and nanofibre morphology) were observed when a non-conducting textile substrate (e.g. polypropylene non-woven) was used as nanofibre collector in multi-nozzle electrospinning. To minimize perturbations, adjustments in the process conditions were studied.

The last challenge is to guarantee adhesion of nanofibres to textiles achieving satisfactory durability for practical uses. Adhesion of nanofibres to textile substrates was characterized by means of peeling tests. Investigations were carried out also for the comprehension of the factors that limit the adhesion. Textile processes, including plasma treatments, were proposed in order to enhance adhesion by pre-treating the textile substrates. In particular, after oxygen low-temperature plasma treatments, a polypropylene non-woven showed significant changes in wettability. The treatments results to increase adhesion energy and force of peeling tests. Adhesion between nanofibres and substrate were about 5-15 times higher for PEO nanofibre when deposited on a plasma treated PP non-woven, and about 2-5 times higher when PA6 nanofibres were used.

The adhesion is low when a fabric composed of staple fibres is used as substrate. Even if treatments could improve the adhesion, optical microscopy observations on both nanofibre layer and fabric after peeling tests suggested that on staple fabrics the electrospun nanofibres were actually linked to few anchor points (i.e. protruding fibre) on the fabric surface. Therefore, surface hairiness of fabrics seems to be a critical limit for considerably improving adhesion, even if improvements can be promoted by the treatments. Hence, not all textile materials are suitable substrates for coating with electrospun nanofibres.

P.33 Electrospinning of keratin/hydroxyapatite nanofibre scaffolds for bone tissue engineering

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Keratin extracted from wool has many useful properties such as biocompatibility and biodegradability [1] and it supports the growth and adhesion of fibroblasts [2] and osteoblasts [3]. Thus, keratin is expected to be applicable for biomedical use in a similar manner to collagen and fibroin. Hydroxyapatite (HA) is used in bone reconstruction although it could not serve alone as bone repair devices because of its weakness in strength. Bones are complex materials composed of proteins with HA, therefore, during the last years many investigations have been focused on hybrid biomaterials of HA with proteins and other synthetic polymers.

Electrospinning process is a low-cost and simple method to produce nanofibrous materials that have particular properties, such as high surface to volume ratio and high porosity, that make them promising candidates for several applications, such as filter membranes, cell-growth, wound dressing and drug delivery. The nanofibres characteristics depend on both the operating conditions of the electrospinning process (flow rate, tension, time, temperature and collector distance) and the properties of the polymer fluid (concentration, solvent, viscosity, conductivity, etc.). In particular, keratin has been electrospun into nanofibres from solutions of formic acid. Unfortunately, HA particles are not stable in acid media, therefore water must be used as solvent. However, electrospinning keratin from water solution is not an easy task. Improved processability can be attained by blending keratin with appropriate polymers, such as polyethylene oxide (PEO). PEO is an amphiphilic, water-soluble, and non-degradable polymer with good biocompatibility and low toxicity. This polymer is often used as an ideal model for the electrospinning process because it can be electrospun without defects from aqueous solutions in a wide range of conditions.

In this work, we carried out electrospinning tests with different keratin/HA water solutions and keratin/PEO/HA blends suitable for the production of composite nanofibrous scaffolds for bone tissue engineering applications.

Keratin was obtained from wool by means of a sulphitolysis extraction method. PEO powder with an average molecular weight Mv = 4 x 10^5 g mol^{-1} was dissolved in distilled water at ambient temperature for about 12 h. The keratin/PEO blend solutions were prepared at room temperature in about 12 h obtaining a total polymer concentration of 7 % w/w with a keratin/PEO weight ratio of 70:30 and adding HA at the concentration of 10% w/w on the keratin content.

Electrospun keratin/PEO/HA nanofibers were subjected to heating treatments in an oven at different temperatures and times in order to assess what are heating temperature and time that give to keratin nanofibers the stability to water. The samples, before and after the heating treatments, were put in deionized water for 24 h in order to study their behavior in water. All samples were characterized by SEM, EDX and FT-IR and the best electrospun mats were tested for osteoblasts cells growth.

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P.34 Biodegradable nanocomposites via electrospinning

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Fibres are used as reinforcement in materials because the smaller the cross sectional area results in strength closer to their theoretical maximum. Fibre mats akin to commercially available pre-impregnated fibres (pre-preg), used in a wide range of industrial applications, can be produced by coaxially electrospinning polymers. By carefully choosing the polymers with different melting points, the fibre mat can then be heated to only melt the shell polymer and form a matrix around the core polymer. Polylactic acid (PLA) and were used are they are both biodegradable, allowing for a completely biodegradable composite to be made. PCL was used as the sheath polymer due to its low melting point of 60 °C, compared to PLA, 160 °C. Three layers of the coaxial fibre mats were melted together, and the tensile properties for this composite were compared to that of a composite made from the same materials, but electrospun separately and assembled with three layers of PLA fibres sandwiched between layers of PCL fibres.

When using similar parameters, results showed that the coaxial, single-step method displayed more repeatable tensile behaviour its layered counterpart. There was however, a decline in properties in the coaxial composite, as yield modulus decreased from 840 MPa to 750 MPa, and ultimate tensile strength decreased from 18.1 MPa to 16.2 MPa. This could have been due to more random alignment of the fibres using the coaxial electrospinning method. Further work was conducted to improve the tensile properties of the coaxial composite by optimising the parameters to attempt increase the alignment and decrease the diameter and variability of the fibres.

P.35 Size dependent mechanical properties of electrospun polystyrene fibres

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Glassy polymers are potentially highly ductile materials and able to fail at relatively large strains. However, the presence of defects in the glassy polymer structure can cause overall brittle behaviour. Polycarbonate is an example of a glassy polymer that contains very few defects in its structure, and is thus used in a range of applications where toughness is required. However, polycarbonate is considered an expensive high performance polymer. Polystyrene (PS) is a considerably cheaper glassy polymer but the structure is typically highly defective, which results in the

characteristic brittle behaviour commonly associated with bulk PS. Conversely, historic work has highlighted the ductility of PS at small length scales [1]. This work therefore exploits electrospinning to produce polystyrene with progressively decreasing fibre diameters for the evaluation of their mechanical properties. Tensile behaviour of individual electrospun PS fibres is performed using novel atomic force microscopy (AFM) in conjunction with scanning electron microscopy (SEM) [2]. The strain to failure and work to fracture of individual PS fibres was observed to increase significantly as the fibre diameter decreased below 1 micron. A theoretical model incorporating polymer chain network organization is used to describe the drawing characteristics of the electrospun PS fibres during tensile testing.

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P.36 Understanding oil repellent mechanisms in electrospun fibre networks

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Electrospun fibre networks have been used extensively to repel liquid water [1, 2] but lower surface tension liquids, especially oils, exhibit a strong tendency to fully wet through the network. This work highlights the importance of fibrous organization and mechanically properties of the individual electrospun fibres, in addition to surface properties, in defining the resultant wetting behaviour between an electrospun fibre network and oil droplets. Our results show a clear dependence between electrospun fibre diameter and the wetting behaviour of oil droplets on the fibrous network, as well as the importance of oil droplet size, using a range of electron and optical microscopy techniques to determine the shape of oil droplets in contact with electrospun fibres. A model based on recent wetting descriptions for simple parallel fibre systems [3] is applied to explain the oil droplet wetting and a definition of a critical droplet volume, above which oil spreading is supressed, is developed. This critical droplet volume is shown to be controlled by the properties of the individual electrospun fibres and their organization within the network. The result of this work is expected to be important in a range of applications where the interaction of liquids in contact with the electrospun fibre networks can be controlled through designed electrospun structures.

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